



## Environmental Management Science Program Research in West Virginia

### West Virginia University

#### **59925 – Modeling of Diffusion of Plutonium in Other Metals and of Gaseous Species in Plutonium-Based Systems**

**Principal Investigator:** Dr. Bernard R. Cooper

**Problem Area:** Deactivation and Decommissioning

The research is aimed at developing and utilizing computational-modeling-based methodology to treat two major problems. The first of these is to be able to predict the diffusion of plutonium from the surface into the interior of another metal such as uranium or stainless steel (fcc iron). The second is the more complicated situation of treating the diffusion of a gaseous species into plutonium-containing oxidized material, specifically the solid-state diffusion of  $O_2$ -driven by an oxygen gradient. Consideration of both problems has arisen out of discussion with scientific staff of the Nuclear Materials Technology Division at Los Alamos National Laboratory. The work will proceed in consultation and cooperation with these LANL personnel. The first class of problem, diffusion of plutonium into host metals is pertinent to characterizing contamination and consequent clean-up procedures in situations where plutonium has been in contact with other metals for extended periods of time. The second situation is pertinent to complicated hydrogen generation mechanisms creating possibly catastrophic pressure in situations, such as storage barrels, where oxidized plutonium containing material has been stored for long periods of time.

The enabling aspect of the study is the availability of atomistic potentials of sufficient physical accuracy to capture the nature of the plutonium interactions in the diffusion process. Therefore the availability of physically accurate ab-initio-based atomistic potentials for plutonium, as well as the host iron or uranium metals, is a key and enabling aspect of this study. Among other things, this allows us to treat thermal effects straightforwardly. Because of this key role of the atomistic potentials, initially we will generate these potentials using two different techniques. B. R. Cooper will initially focus on the first of these and G. W. Fernando on the second. We will then select one of the two methods as based on testing of accuracy in comparison to some of our existing fully quantum mechanical calculations and experiment and also, if the two methods provide essentially equally accurate atomistic potentials, as based on computational efficiency. The first method has the strength of our being able to phenomenologically tailor it to include what we perceive to be the key physics of plutonium-based systems, while the second method has the strength of complete objectivity in the information inserted. This second method does, however, depend on inputting the large amount of information needed by use of pseudopotential techniques; and it remains for us to test how well this works for plutonium-based systems.

The two methods for generating interatomic potentials involve: (1) A new technique for constructing many-body atomistic potentials based on ab initio total energy data, starting from a formal expansion of total energy as motivated by Generalized Pseudopotential Theory (GPT). Because of the wide range of deformation energetics included in these calculations, the resulting potentials are expected to provide a more realistic description of materials under large deformation than potentials fitted to physical properties

predominantly near equilibrium. (2) Methodology based on the synthesis of a maximum entropy method and total energy calculations; we will generate a large number of configurations with their total energies, as needed for this second method, by the use of plane-wave pseudopotential in Car-Parrinello type dynamics on cells containing a few hundred atoms. The two potential generation methods will be tested in modeling applications by a side-by-side comparison with each other, with *ab initio* Local Density Approximation (LDA) calculations insofar as possible, and with experiment. These properties will include ones demonstrating transferability of the potentials. We will use the testing and comparison to select one of the two potential generation methods for use in the diffusion calculations. This selection will be on the basis of computational efficiency in generating a potential of comparable physical quality and/or of providing a potential clearly superior in incorporating the physical information. If doubtful of any results, we will always have the option of repeating any calculations using the atomistic potential obtained by the other means.

B. R. Cooper and people working with him at West Virginia University have been actively engaged over the past five years in developing such potentials for *d* transition metals as well as for simple metals. These potentials have been obtained from a data base consisting of full-potential totally energy calculations, using previously developed capabilities for a substantial number of crystallographic configurations. At present, B. R. Cooper, who is a consultant at LANL, is serving as postdoctoral mentor to J. D. Becker, a LANL postdoctoral, who is using *ab initio* force techniques to study lattice relation in supercells containing 32 atoms, e.g. 31 plutoniums and 1 gallium. (This force technique was developed by J. M. Wills of LANL as an outgrowth of the full-potential total energy technique previously developed by J. M. Wills and D. L. Price working with B. R. Cooper at West Virginia University.) The total energies generated at the intermediate and final steps of this procedure, as well as total energies for other lattice configurations will provide the data base used in the first method for extracting the plutonium atomistic potentials.

The investigation of thermally-activated diffusion will make use of transition state theory with dynamic corrections. In transition state theory the number of crossings of a specified counting surface that separates initial and final states is equated to the number of such crossings that occur in an equilibrium system. The use of *ab-initio*-based atomistic potentials will allow us to efficiently map out the pertinent energy barriers. Molecular dynamics can be used to treat realistically the nature of the hoppings as well as to correct for dynamical effects such as recrossings. As guided by experiment, we will use our experience in simulating grain boundaries and incorporating them in dynamic simulations to study the relative importance of grain boundary diffusion in allowing plutonium atoms to penetrate into the interior of the host metals.

Having described the overall nature of the modeling calculations, we will now give further details on the two main components of the modeling study. These are: (1) the treatment of diffusion and of the pertinent grain boundary modeling and (2) the development of physically accurate plutonium atomistic potentials. The physical quality of these potentials is apt to be the controlling quantity in determining the ability to be accurately predictive for the questions of interest.

## **Annual Progress Reports**

**1998 Progress Report**

**1999 Progress Report**

**2000 Progress Report**

**2001 Progress Report**

# **Environmental Management Science Program Research in New Mexico**

## **Sandia National Laboratories – New Mexico**

### **60363 – Optimization of Thermochemical, Kinetic, and Electrochemical Factors Governing Partitioning of Radionuclides during Melt Decontamination of Radioactively Contaminated Stainless Steel**

**Principal Investigator:** Dr. James A. Van Den Avyle

**Problem Area:** Deactivation and Decommissioning

Melt Decontamination represents an effective scrap metal recycling route for the estimated 1,200,000 tons of contaminated stainless steel and nickel currently within the DOE complex. At present, this material must be considered a substantial disposal liability. However, with appropriate recycling, this material may be regarded as an asset worth an estimated \$5 billion. The DOE anticipated buying 6.2 million tons of stainless steel for use as waste burial containers. The proposed outcome of this work would eliminate the need for many of those containers while providing the material for the remainder. The conversion of a disposal liability into a final product (which DOE already plans to purchase) reduces the volume of material necessary for burial and saves billions of dollars in material costs.

The goal of this project is to optimize a melt decontamination process through a basic understanding of the factors which govern the partitioning of various radionuclides between the metal, slag, and gas phases. Radionuclides which are captured by a slag phase may be stabilized by promoting the formation of synthetic minerals within a leach resistant matrix. This research describes an integrated program of simulation and experimentation designed to investigate and optimize liquid metal techniques for the decontamination and recycling of radioactive scrap metal. This program will combine Sandia expertise and ongoing work in fundamental separation science and liquid metal processing technology via a focused effort aimed at understanding the thermodynamic, electrochemical, and kinetic reactions which occur within melt refining processes. The goal of this work is to apply a broad range of Sandia capabilities and experience towards the development of a viable method to decontaminate and recycle high value metals currently within the DOE complex, as well as stabilizing and significantly reducing the volume of radioactive contaminated waste in need of disposal. While melt decontamination of radioactive contaminated metals has been previously studied, this work represents the first comprehensive effort to understand and optimize the driving forces which govern decontamination by means of radionuclide partitioning.

## **Annual Progress Reports**

**1998 Progress Report**

**1999 Progress Report**

# **Environmental Management Science Program Research in Tennessee**

## **Oak Ridge National Laboratory**

### **64896 – Decontamination of Radionuclides from Concrete During and After Thermal Treatment**

**Principal Investigator:** Dr. Brian P. Spalding

**Problem Area:** Deactivation and Decommissioning

The total area of contaminated concrete within all DOE facilities is estimated at  $7.9 \times 10^8 \text{ft}^2$  or approximately 18,000 acres with the major contaminating radionuclides being U,  $^{90}\text{Sr}$ ,  $^{60}\text{Co}$ , and  $^{137}\text{Cs}$  (Dickerson et. al. 1995). Techniques to decontaminate concrete through the application of heat (including microwaves, infrared radiation, lasers, plasma torch, etc.) have centered on the generally known deterioration of concrete strength with imposed thermal stress. These strategies have all attempted to spall or scabble contaminated solids from the concrete surface and to maximize the particular technology's capability to that end. However, in addition to the imprecisely defined knowledge of the physical effects of specific heat treatments on concrete (final temperature, heating rate, and type of concrete aggregate), concomitant behavior of DOE's major radioactive contaminants ( $^{137}\text{Cs}$ , U,  $^{90}\text{Sr}$ , and  $^{60}\text{Co}$ ) during thermal treatment is very poorly known. The proposed research will determine the thermal effects between 100 and 1400EC on concrete engineering properties (compressive strength, strain, porosity, bulk density, and cracking), chemical properties (dehydration, mineral phase change, and solubility), and contaminant behavior as a function of final temperature, heating rate, and aggregate type (none, limestone, or silica); thermal effects on contaminants and concrete are depicted conceptually in Figure 1. Major effects on radionuclide transport via direct volatilization (particularly for  $^{137}\text{Cs}$  and  $^{60}\text{Co}$ ) during heating are anticipated to lead to in situ decontamination techniques. Changes in the extractability of radionuclides from heat affected concrete will be measured, using short-lived radioisotopes, to ascertain changes in decontamination potential following thermal treatment. Detailed finite-element modeling of heat flow in concrete and resulting mechanical stresses (from pore pressure and thermal expansion) of optimal thermal treatments will be completed so that effects on laboratory-sized specimens can be extrapolated to field-scale thermal treatments on concrete mechanical properties and contaminant behavior. Expected results of the proposed research will be a thorough and detailed understanding of the thermal effects on concrete engineering properties and concomitant radionuclide behavior including a detailed empirical data base. Specific decontamination technologies using thermal stressing of concrete will then be able to predict their effects rather than continue with DOE's apparent present approach of supporting novel thermal technologies without either a basic understanding of the limits of thermal effects on concrete or the fate and behavior of key radionuclides.

## **Annual Progress Reports**

[\*\*1999 Progress Report\*\*](#)

[\*\*2000 Progress Report\*\*](#)

[\*\*2001 Progress Report\*\*](#)

# **Environmental Management Science Program Research in Tennessee**

## **Oak Ridge National Laboratory**

### **64912 – Improved Decontamination: Interfacial, Transport, and Chemical Properties of Aqueous Surfactant Cleaners**

**Principal Investigator:** Dr. David W. DePaoli

**Problem Area:** Deactivation and Decommissioning

This investigation is focused on decontamination using environmentally benign aqueous solutions, specifically the removal of organics and associated radionuclide and heavy metal contaminants by synthetic surfactants. Aqueous-based solutions promise several advantages for decontamination processes, including low hazard potential, low cost, and reduced secondary waste volume through solvent recycle, solvent degradation, and/or incineration.

The work aims at gaining an understanding of interfacial, transport, and chemical processes that govern the effectiveness of aqueous-based surfactant solutions for decontamination of surfaces. Specific goals of the work include the elucidation of:

- C dynamics of aqueous surfactant wetting and contaminant removal,
- C basic knowledge of surfactant diffusion/adsorption on surfaces,
- C effects of interfacial properties on effective surfactant application to surfaces, and
- C means for separation of waste materials from aqueous-based cleaning materials.

The understanding developed in this work will be directly applied to decontamination/decommission tasks by testing surface samples from DOE contaminated sites (such as those from the enrichment process building of K-25 site) and will provide the basis for improved approaches for removal of organic contamination by synthetic surfactants. These improvements will lead to decreased hazards for workers, decreased secondary waste generation, increased efficiency, and lower cost.

The proposed research program is a multi-disciplinary and multi-institutional collaboration between a national laboratory and a university. The team includes engineers and scientists with expertise in colloid and interfacial phenomena and separation processes.

## **Annual Progress Reports**

**1999 Progress Report**

**2000 Progress Report**

**2001 Progress Report**

# **Environmental Management Science Program Research in Washington**

## **Pacific Northwest National Laboratory**

### **64947 – Contaminant-Organic Complexes, Their Structure and Energetics in Surface Decontamination Processes**

**Principal Investigator:** Dr. Calvin C. Ainsworth

**Problem Area:** Deactivation and Decommissioning

The DOE must decontaminate and decommission a large number of surplus facilities. At present there are about 7,000 contaminated facilities that require deactivation and decommissioning. A major need associated with this effort is improvement of metal surface decontamination. The DOE is responsible for and disposal of approximately 180,000 metric tons of metal (mostly steel) associated with their nuclear facilities. Much of this metal is steel and iron which develops a passivity layer where radionuclides and other contaminants are retained. Continued deposition of corrosion products on the steel surfaces allows radioactive materials to be continually sorbed to these secondary oxide layers, incorporated into their structure or occluded by overgrowth.

This project will investigate the use of powerful, microbially produced chelates (termed siderophores) as decontamination and sequestering agents. Studies of these compounds demonstrate that their binding affinity for Fe and actinides(IV) are as much as 20 orders of magnitude higher than other chelating agents (i.e., EDTA). Siderophores evolved because living organisms require Fe which in the natural environment is extremely insoluble. The central research tenets are that the siderophores will readily dissolve oxides from steel surfaces, corrosion pits and cracks and solubilize the associated contaminants, that their high binding affinity will sequester Fe and Actinide(IV) species against adsorption to the cleaned metal surface, that structure-reactivity relationships will allow the selection of optimum siderophore structures/conditions for use, and will decrease the generation of secondary waste.

The research integrates studies of macroscopic dissolution of U and Fe oxides with molecular spectroscopy (FTIR, Raman, EXAFS), to probe the structure and bonding of the siderophores and their functional moieties and how these change with the chemical environment, and with molecular mechanics and electronic structure calculations designed to model siderophore structure-reactivity relationships. Our goals are 1) to develop the fundamental knowledge necessary to relate the chemistry of contaminated oxide dissolution and metal sequestration by siderophore, and 2) to develop the information necessary to tailor siderophore structure and properties to EM's disparate metal surface decontamination needs.

## **Annual Progress Reports**

**1999 Progress Report**

**2000 Progress Report**

# **Environmental Management Science Program Research in Illinois**

## **Argonne National Laboratory**

### **64965 – Supercritical Carbon Dioxide-Soluble Ligands for Extracting Actinide Metal Ions from Porous Solids**

**Principal Investigator:** Dr. Mark L. Dietz

**Problem Area:** Deactivation and Decommissioning

The objective of this project is to develop novel, substituted diphosphonic acid ligands that can be used for supercritical carbon dioxide extraction (SCDE) of actinide ions from solid wastes. These ligands will be used to investigate fundamental aspects of metal extraction into supercritical fluids. Diphosphonic acid ligands, which form extremely stable complexes with actinide metal ions in aqueous and organic solution, will be made soluble in supercritical carbon dioxide by the introduction of alkyl or poly(dimethylsiloxane) substituents. Ligands with these functional groups are less expensive than those with the fluorinated substituents customarily used to enhance solubility. This project consists of three steps: synthesis of the ligands, exploration of the basic metal complexation chemistry of the ligands in supercritical carbon dioxide, and development of techniques for SCDE of actinide ions from porous solids.

## **Annual Progress Reports**

**1999 Progress Report**

**2000 Progress Report**

**2001 Progress Report**

# **Environmental Management Science Program Research in Pennsylvania**

## **University of Pittsburgh**

### **65001 – Development of Novel, Simple, Multianalyte Sensors for Remote Environmental Analysis**

**Principal Investigator:** Dr. Sanford A. Asher

**Problem Area:** Deactivation and Decommissioning

We will develop simple, inexpensive new chemical sensing materials which can be used as visual color test strips to sensitively and selectively report on the concentration and identity of environmental pollutants such as cations of Pb, U, Pu, Sr, Hg, Cs, Co as well as other species. We will develop inexpensive chemical test strips which can be immersed in water to determine these analytes in the field. We will also develop arrays of these chemical sensing materials which will be attached to fiber optic bundles to be used as rugged multichannel optrodes to simultaneously monitor numerous analytes remotely in hostile environments.

These sensing materials are based on the intelligent polymerized crystalline colloidal array technology we recently developed. This sensing motif utilizes a mesoscopically periodic array of colloidal particles polymerized into an acrylamide hydrogel. This array Bragg diffracts light in the visible spectral region due to the periodic array of colloidal particles. This material also contains chelating agents for the analytes of interest. When an analyte binds, its charge is immobilized within the acrylamide hydrogel. The resulting Donnan potential causes an osmotic pressure which swells the array proportional to the concentration of analyte bound. The diffracted wavelength shifts and the color changes. The change in the wavelength diffracted reports on the identity and concentration of the target analyte.

Our successful development of these simple, inexpensive highly sensitive chemical sensing optrodes, which are easily coupled to simple optical instrumentation, could revolutionize environmental monitoring. In addition, we will develop highly rugged versions, which can be attached to core penetrometers and which can be used to determine analytes in buried core samples.

## **Annual Progress Reports**

### **1999 Progress Report**

### **2000 Progress Report**



# **Environmental Management Science Program Research in California**

## **University of California, Los Angeles**

### **73835 – Atmospheric-Pressure Plasma Cleaning of Contaminated Surfaces**

**Principal Investigator:** Dr. Robert F. Hicks

**Problem Area:** Deactivation and Decommissioning

A basic research program is proposed on the plasma etching of heavy metals. We have invented an atmospheric-pressure plasma source for decontamination and decommissioning of nuclear wastes. This source is a tremendous advancement over previous plasma technologies, because it may be easily deployed at the site requiring decontamination. With our source, tantalum (a plutonium surrogate) has been etched at rates up to  $6.0 \pm 0.5 \mu\text{m}/\text{min}$ . By adding fluorine-containing compounds to the gas, the atmospheric-pressure plasma may be used to strip a wide range of radioactive elements from contaminated structures and equipment. Furthermore, the source design has been greatly improved so that it is compact, rugged, reliable, and easily configured to treat objects of different sizes and shapes. We have identified seven Environmental Management Needs from the EM-NMS list that could significantly benefit from our technology. These are AL-09-01-12-DD, ID-7.2.25, ID-7.2.26, ORDD-02, RL-DD02, RL-DD03, and SR00-4015. Potentially, additional EM Needs could be addressed with further advancements in the plasma source. The objectives of our research program are to fully characterize the discharge physics and chemistry, to engineer the exhaust containment system, and to test the plasma device on contaminated structures within the Department of Energy complex. Through a joint effort between the University of California, Los Angeles (UCLA) and Los Alamos National Laboratories (LANL), we will surmount the remaining scientific hurdles to implementation. Moreover, we will collaborate with personnel at LANL and at INEEL to demonstrate the technology in the field. By supporting this project, the Department of Energy will ensure that the full potential of this new plasma process will be brought to bear on Environmental Management's D&D programs.

## **Annual Progress Report**

### **2001 Progress Report**

### **2002 Progress Report**

# **Environmental Management Science Program Research in Washington**

## **Pacific Northwest National Laboratory**

### **82715 – Development of Biodegradable Isosaccharinate-Containing Foams for Decontamination of Actinides: Thermodynamic and Kinetic Reactions between Isosaccharinate and Actinides on Metal and Concrete Surfaces**

**Principal Investigator:** Dhanapat Rai

**Problem Area:** Deactivation and Decommissioning

Actinide contamination of steel and concrete surfaces is a major problem within the DOE complex. For steel surfaces, the primary problem is contamination of sections of nuclear power reactors, weapons production facilities, laboratories, and waste tanks. For concrete, there are an estimated 18,000 acres of concrete contaminated with radioactive materials that need decontamination. Significant efforts have gone into developing decontamination technologies. Almost all current decontamination technologies rely on removal of the contaminated surface layer either by mechanical means or chemical methods using harsh chemicals. Some of the technologies are ineffective. Others are expensive, labor intensive, and hazardous to workers. Still others create secondary mixed wastes that are not environmentally acceptable.

This proposed project seeks fundamental information that will lead to the development of a new and more environmentally acceptable technology for decontamination of Pu on steel and concrete surfaces. The key component of this technology is isosaccharinate (ISA), a degradation product of cellulose materials that is biodegradable and binds strongly with Pu. Isosaccharinate will be incorporated into foams for use in decontamination of Pu from steel and concrete surfaces. To develop a fundamental basis for this proposed technology, we will 1) study the effect of pH and common ions (Na, Ca) on the speciation and thermodynamic reactions of ISA over wide ranges of pH and concentrations of Na and Ca, 2) develop thermodynamic and kinetic data for ISA reactions with Pu(IV) and Fe(III), and 3) determine the fundamental Pu concentration-controlling reactions involving steel and concrete surfaces and test contaminated surfaces using ISA-containing foams for Pu removal. Our ultimate goal is to develop a technology, based on sound fundamental principles, for decontaminating tetravalent actinides. The proposed research is a multi-laboratory effort including fundamental chemistry studies being conducted at Pacific Northwest National Laboratory and Lawrence Berkeley National Laboratory, and foam formulation and decontamination research at Sandia National Laboratories.

## **Annual Progress Reports**

### **2002 Progress Report**

# **Environmental Management Science Program Research in Illinois**

## **Argonne National Laboratory**

### **82723 – Remote Manipulation for Deactivation and Decommissioning Exhibiting Tele-Autonomy and Tele-Collaboration**

**Principal Investigator:** Thomas Yule

**Problem Area:** Deactivation and Decommissioning

The liability for deactivation and decommissioning (D&D) of contaminated structures in the weapons complex is about \$30 billion. Remote systems will be essential for this work to reduce risk to human workers from hazardous radiation and difficult work environments, while improving productivity and reducing costs. The proposed work focuses on enhancing remote operation of tools for D&D tasks by extending teleoperation with semi-autonomous functions. This work builds on preliminary work done on a reactive, agent-based control architecture, which is well suited to unstructured and unpredictable environments, and *cobot* control technology, which implements a virtual fixture that can be used to guide the application of tools with force-feedback control. Developed methodologies will be tested using simulation, and then implemented using a structured light sensor and cobot hand controller on a dual-arm system to measure the enhanced performance of key tool operations that are tedious and difficult to perform purely by teleoperation. The collaboration of Argonne National Laboratory (ANL) and Northwestern University (NWU) blends capabilities in applied and basic research, addressing one of the RFP's goals of bridging the gap between broad fundamental research and applied technology development focused on D&D. This work significantly leverages some 2000 hours of operational experience gained during the D&D of the CP-5 reactor at ANL using a dual-arm remote manipulator system, as well as DOE's \$1.2M investment in the dual-arm system itself, which will serve as a test bed for the proposed investigations.

## **Annual Progress Reports**

### **2002 Progress Report**

# **Environmental Management Science Program Research in Washington, District of Columbia**

## **Naval Research Laboratory**

### **82749 – Field Portable Microchip Analyzer for Airborne and Surface Toxic Metal Contaminants**

**Principal Investigator:** Greg Collins

**Problem Area:** Deactivation and Decommissioning

This proposal is being written as a competitive renewal of a proposal funded under the Office of Energy Research Notice 98-04, entitled, “Metal Ion Analysis Using Near-infrared Dyes and the Laboratory-on-a-Chip” (Project ID Number: 64982). The primary research objective of this competitive renewal is to develop a portable, capillary electrophoresis microchip capable of sensitively and rapidly monitoring hazardous waste metal ions critical to the successful deactivation and decommissioning (D&D) of contaminated equipment and structures at various DOE sites. This work will allow us to extend the capabilities of the microchip beyond the presently demonstrated capabilities for monitoring low ppb levels of uranium (VI), to hazardous waste metal ions which include  $\text{Be}^{2+}$ ,  $\text{Cr}^{6+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cs}^+$ , and  $\text{Sr}^{2+}$ . As an integral part of this effort, particular emphasis will be placed on developing viable, new extraction methods for metal ion sampling from both the air via a microimpinger which is integrated onto the microchip itself, and from contaminated surfaces, both techniques being amenable to on-line introduction onto the microchip. In order to simultaneously quantitate the various hazardous waste metal ions highlighted here, a new microchip design capable of performing parallel electrophoretic separations in a single extraction sample is presented, each microchannel employing its own uniquely developed separation medium. Two different detection methods for monitoring the electrophoretic separations taking place down the microchannel will be exploited in this proposal, indirect and direct detection. Special emphasis has been placed on maintaining the ultimate portability of a final microchip device through the careful selection of metallochromic dyes and fluorophores which are amenable to use of small, inexpensive light sources (e.g., LED's) and photodetectors.

## **Annual Progress Reports**

### **2002 Progress Report**

# **Environmental Management Science Program Research in Washington**

## **Pacific Northwest National Laboratory**

### **82773 – Contaminant-Organic Complexes: Their Structure and Energetics in Surface Decontamination Processes**

**Principal Investigator:** Calvin C. Ainsworth

**Problem Area:** Deactivation and Decommissioning

Proposed research will extend the scientific understanding of powerful, microbially produced chelates (siderophores) and newly developed information resulting from a FY98 EMSP project by further investigating the use of siderophores and siderophore-like designed chelates as decontamination and sequestering agents. The DOE must decontaminate and decommission a large number of surplus facilities. At present there are about 7,000 contaminated facilities that require deactivation and decommissioning. A major need associated with this effort is improvement of metal surface decontamination. The DOE is responsible for and disposal of approximately 180,000 metric tons of metal (mostly steel) associated with their nuclear facilities. Much of this metal is steel and iron, which develops a passivity layer where radionuclides and other contaminants are retained. Continued deposition of corrosion products on the steel surfaces allows radioactive materials to be continually sorbed to these secondary oxide layers, incorporated into their structure, or occluded by overgrowth. The central tenets of this research are 1) natural- and designed-siderophores will readily dissolve oxides from steel surfaces, corrosion pits and cracks and solubilize the associated contaminants, 2) siderophores' high binding affinity will sequester Fe and actinide(IV) species against adsorption to the cleaned metal surface, 3) structure-reactivity relationships will allow the selection of optimum siderophore structures/conditions, and 4) the use of these chelates will decrease the generation of secondary waste and increase the efficiency of decontamination.

Studies of these compounds demonstrate that their binding affinity for Fe and actinides(IV) are as much as 20 orders of magnitude higher than other chelating agents (i.e., EDTA). During our previous EMSP investigations, the hydroxamate-type siderophores rapidly dissolve Fe(III) oxides common to corrosion products (hematite and maghemite). Oxide morphology tended to effect dissolution rate. The presence of Cr substitution as mixed Fe, Cr-oxides influenced hematite dissolution. Sorbed surrogate actinides (thorium IV and europium LII) were readily desorbed from the surface in the presence of siderophores. Aging >1 yr did not influence the local coordination chemistry of sorbed actinide surrogates (Eu and Nd), allowing us to extrapolate information from our short-term laboratory measurements to long-term field environments. All of these results occurred in the absence of harsh acidic or caustic conditions common to currently used decontamination and sequestering techniques. Previous modeling efforts have resulted in the development of a MM3 model for the catecholamide-type siderophores and suggests these chelates will function as superior chelates for decontamination.

The continued research proposed herein integrates 1) studies of macroscopic dissolution/desorption of common actinide (IV) species (U, Pu, and Np) and Fe oxides, 2) molecular spectroscopy (Fourier Transform Infrared Spectroscopy, Raman, X-ray Absorption Spectroscopy), to probe the structure and bonding of the siderophores and their functional moieties and how these change with the chemical environment, and 3) molecular mechanics and electronic structure calculations can be utilized to design model siderophore compounds for decontamination. Our goals are 1) to develop the fundamental knowledge necessary to relate the chemistry of contaminated oxide dissolution and metal sequestration by siderophores, and 2) to develop the information necessary to tailor catecholamide-type siderophore structures and properties to EM's disparate metal surface decontamination needs.

## **Annual Progress Reports**

### **2002 Progress Report**

## **Environmental Management Science Program Research in California**

### **Lawrence Livermore National Laboratory**

#### **82784 – Assessing the State and Distribution of Radionuclide Contaminants in Concrete: An Experimental and Modeling Study of the Dynamics of Contamination**

**Principal Investigator:** Brian Viani

**Problem Area:** Deactivation and Decommissioning

There are hundreds of cement structures in the DOE complex that are contaminated by radionuclides and other chemicals. A fundamental understanding of the factors governing contaminant interactions in concrete is necessary in order to evaluate and model contaminant transport and develop more efficient methods for D&D efforts. The goal of this research is to enhance our understanding of how radionuclides bind to concrete and to develop a more accurate predictive capability which will allow various decontamination approaches to be evaluated. This will be accomplished through a combination of laboratory-based experiments on radionuclide interactions with cementitious materials, along with state-of-the-art materials characterization and transport modeling techniques. Transport studies including flow-through and batch sorption tests will be initiated using the radionuclides Cs, Tc, U, and Pu and ordinary Portland cement with or without aggregates. In addition to standard radioanalytical and microscopic methods, X-ray absorption spectroscopy will be used to provide detailed, element-specific information on radionuclide speciation, including distribution, redox activity, and aging effects. Results from these experiments will be compared to characterization of actual aged concrete cores from contaminated DOE facilities. Transport modeling simulations will use the chemical parameters determined from the lab-based experiments and the materials characterization tasks to predict the depth of contaminant penetration and its chemical form and association in the concrete. Our simulations explicitly account for fracture flow and mineralogical heterogeneity and will be used to predict the effect of fractures and aggregate on the resulting radionuclide distribution. The team assembled here has extensive background and experience in studying radionuclide interactions with cementitious materials.

**This project began in 2001. The first progress report is expected in late 2003.**

# **Environmental Management Science Program Research in Tennessee**

## **Oak Ridge National Laboratory**

### **82792 – Alternative Ionization Methods for Particle Mass Spectrometry**

**Principal Investigator:** William Whitten

**Problem Area:** Deactivation and Decommissioning

The purpose of this project is to explore enhanced ionization techniques for real-time mass spectrometry of individual airborne particles. We have developed an instrument for aerosol analysis based on laser ablation ion trap mass spectrometry. While the method is extraordinarily sensitive for substances of low ionization potential (IP) such as uranium in most matrices, results are less favorable for elements of higher IP such as mercury and sensitivity for all analytes is highly matrix-dependent. We propose to use resonance ionization together with laser ablation to reduce the effects of charge exchange during the laser ablation expansion plume and thus improve the ionization efficiency for high IP analytes. Glow discharge ionization will also be studied as a means to obtain negative ions from substances with high electron affinity such as PCBs and dioxins. These ionization techniques should improve sensitivity and eliminate the matrix effects that inhibit quantitation. The resulting instrument would have many D&D applications, monitoring in real time for airborne particles containing actinides, technetium, mercury, and chlorinated organic compounds. The sensitivity for these substances should be much higher than can be attained by radiation counting or other conventional methods.

## **Annual Progress Reports**

### **2002 Progress Report**

# **Environmental Management Science Program Research in Tennessee**

## **Oak Ridge National Laboratory**

### **82794 – Multi-Optimization Criteria-Based Robot Behavioral Adaptability and Motion Planning**

**Principal Investigator:** Francois G. Pin

**Problem Area:** Deactivation and Decommissioning

To save significant amounts of time and cost in performing the wide variety of manipulative tasks required by D&D operations, the future generation of D&D robots will likely require practical modularity and kinematics redundancy (more-than-6-dof articulated chains), either as mobile manipulators or dual-arm systems. Several basic research issues remain unsolved for these systems, in particular with respect to motion planning with (1) “on-the-fly” adaptability to changes in task objectives and conditions, (2) complete changes in kinematics configuration, or (3) tasks characterized by multi-criteria objectives (high precision, high payload, obstacle avoidance, hydraulic flow minimization, etc.). To address these issues which put severe limitations on the current generation of D&D robots, we propose to develop a general joint motion planning methodology that permits: 1) no restriction on the number or type of joints, constraints, or task objectives, and 2) “on-the-fly” behavioral adaptability to changes in task objectives and conditions, including multiple, and multiple types of, criteria and constraints. In order to address this very wide class of systems, our approach proposes a radically new avenue for optimization-based resolution of under-specified systems of algebraic equations with constraints. Simulations of existing ORNL test-bed robots will be used in proof-of-principle experiments to illustrate the developed methodologies and algorithms and support subsequent transitions to existing and future D&D robots.

## **Annual Progress Reports**

### **2002 Progress Report**



# **Environmental Management Science Program Research in Tennessee**

## **Oak Ridge National Laboratory**

### **82797 – Image-Based Visual Servoing for Robotic Systems: A Nonlinear Lyapunov-Based Control Approach**

**Principal Investigator:** Warren E. Dixon

**Problem Area:** Deactivation and Decommissioning

Most of the current visual servoing research exploits the assumption of a perfectly calibrated camera, so that a measurable relationship exists between the position of an object in the camera-space and the task-space. This relationship is necessary to utilize the camera information to develop a control input signal to the robotic system. However, if the camera is not perfectly calibrated the information provided to the actuator-level controller will be erroneous, leading to poor tracking performance. This research proposes to develop a new approach for visual servoing that adapts for the unknown camera calibration parameters (e.g., focal length, scaling factors, camera position and orientation) and the physical parameters of the robotic system (e.g., mass, inertia, friction). The basic idea is to use nonlinear Lyapunov-based techniques to overcome the complex control issues and alleviate many of the restrictive assumptions that impact current robotic applications. The resulting outcome of this control methodology will be a plug-and-play visual servoing control module that can be utilized in conjunction with current technology such as feature extraction and recognition, to enable current EM robotic systems with the capabilities of increased accuracy, autonomy, and robustness, with a larger field of view (and hence a larger workspace). These capabilities will result in a significant schedule acceleration and cost reduction of D&D operations while reducing the risk of danger to humans. The developed visual servoing control module will be demonstrated through simulations and a series of experimental proof-of-principle demonstrations on current ORNL robotic systems.

## **Annual Progress Reports**

### **2002 Progress Report**

## **Environmental Management Science Program Research in Tennessee**

### **Oak Ridge National Laboratory**

#### **82799 – Bio-Chemo-Opto-Mechanical (BioCOM) Sensors for Real-Time Characterization**

**Principal Investigator:** Thomas Thundat

**Problem Area:** Deactivation and Decommissioning

Basic and applied research will be conducted to develop simple to use chemical and biological sensor chips utilizing bio-chemo-mechanics for real-time, in-situ, detection of technetium, mercury, uranium, and beryllium in solution for deactivation and decommissioning applications. The bio-chemo-opto-mechanical (BioCOM) chip involves properly fashioned arrays of micromachined silicon cantilevers containing embedded deformable diffraction gratings functionalized with chemically selective coatings. Adsorption of specific molecules on the cantilever array leads to bending, which changes the diffraction of light resulting in a change of color. The bio-chemo-opto-mechanical (BioCOM) chips that will contain an array of pixels, with each pixel containing an array of microcantilever springs in which one surface is derivatized with either an antibody coating or a self-assembled monolayer (SAM) coating for detecting Hg, Be,  $\text{UO}_2^{2+}$  or  $\text{TcO}_4$ . The proposed sensors would not require any external power, external or onboard electronics, or fluorescent dyes and associated optics, which will keep its fabrication and operation costs low while making it simple to use in real-time environmental monitoring. In addition to high sensitivity and miniature size, the BioCOM sensor platform also offers the luxury of simultaneous measurement of many analytes using a single chip.

### **Annual Progress Reports**

#### **[2002 Progress Report](#)**

# **Environmental Management Science Program Research in Tennessee**

## **Oak Ridge National Laboratory**

### **82803 – Innovative Laser Ablation Technology for Surface Decontamination**

**Principal Investigator:** Winston C.H. Chen

**Problem Area:** Deactivation and Decommissioning

It is known that both radioactive and non-radioactive contamination on metal and concrete structures at DOE facilities are found mostly on the surfaces. Safe removal of these contaminants from these surfaces is a critical need. We propose an innovative approach for the safe removal of surface contaminants by using Laser Ablation Decontamination in Liquid (LADIL). With LADIL, laser irradiation is applied to surfaces immersed in liquid. The desorbed contaminants, especially radionuclides, can be confined within a much smaller volume which can be subsequently disposed of. In this project, we will conduct a laboratory demonstration of surface decontamination by LADIL. In addition, we will also determine the optimum conditions for efficient surface decontamination.

The laser ablation process has been broadly used for desorption of materials on surfaces in laboratories. In the typical application of this approach, a surface to be treated is irradiated by a laser beam, which causes the evaporation of a thin surface layer into gas phase. However, the use of laser ablation to remove contaminants into air can cause serious health concerns for workers. Since radionuclides and heavy metals can be easily re-adsorbed on surfaces in the surrounding area, secondary wastes can also be produced. With LADIL, the evaporated materials are confined in the solvent such that the secondary pollution can be totally eliminated. The efficiency is expected to be greater than laser removal techniques in air.

Currently, gaps exist in the knowledge base for the mechanism of laser ablation at the liquid-solid interface. We will pursue the basic understanding of surface heating as well as formation and collapse of micro-bubbles during the laser ablation process. We will study the detailed mechanisms of laser induced desorption of radionuclides, cluster formation and precipitation processes of radionuclides to provide the knowledge base necessary to achieve efficient and safe removal of contaminants on a large scale.

## **Annual Progress Reports**

### **2002 Progress Report**

# **Environmental Management Science Program Research in Tennessee**

## **Oak Ridge National Laboratory**

### **82807 – Physico-Chemical Dynamics of Nanoparticle Formation during Laser Decontamination and Characterization**

**Principal Investigator:** Meng-Dawn Cheng

**Problem Area:** Deactivation and Decommissioning

Advances in compact miniaturized solid-state laser, intensified detector, and digital signal processing in the past few years have made the development of cost-effective innovative field-portable photonics technology for DOE D&D applications highly possible. Plasma induced by a pulsed laser (laser-induced plasma or LIP) can potentially be utilized for clean up of contaminated surfaces and for characterization of surface-bounded contaminants such as heavy metals and radionuclides, simultaneously. Enormous number of ions and nuclei are produced as a result of the extremely transient mass and energy transfer processes. Particles will be generated from such processes and play a key role in the success of the decontamination and/or characterization. To improve our understanding of the particle production processes and the dynamics of particles, real-time physico-chemical characterization is needed. We propose to investigate nanoparticle formation and growth dynamics by conducting experiments on surfaces to be obtained from a contaminated site and those prepared in our laboratories at the Oak Ridge National Laboratory (ORNL). Effects of laser characteristics on nanoparticle formation and dynamics will be examined. These processes will be studied by characterizing the size of nanoparticles in real time using a new fast-scan ( $< 1$  s) nano-differential mobility particle analyzer to be developed in the first year. The real-time particle chemistry will be observed using the aerosol beam focused laser-induced plasma spectrometry first developed by ORNL. A model will be developed to simulate the formation and growth process of nanoparticles produced by the LIP processes. The results to be obtained in this research project will enable EM to design an advanced technology for simultaneous characterization (using time-resolved aerosol spectroscopy) and decontamination (using laser-induced plasma). The knowledge about nanoparticle formation and dynamics will enable the technology development to be optimized. The knowledge on the physico-chemical properties of particles will enable EM to design a better and safer approach in protecting D&D workers from exposure to airborne particles laden with heavy metals and radionuclides in a size range (nanometers) that has high penetration efficiency to human lungs and most respiratory protection gears.

## **Annual Progress Reports**

### **2002 Progress Report**

# **Environmental Management Science Program Research in Tennessee**

## **Oak Ridge National Laboratory**

### **82810 – Hybrid Actuators for Enhanced Automation in D&D Systems Tasks**

**Principal Investigator:** John F. Jansen

**Problem Area:** Deactivation and Decommissioning

Currently, teleoperated manipulators and vehicles dominate DOE's D&D remote systems work. The greatest impact on D&D remote systems work could arise if conventional teleoperated systems could be replaced with semiautonomous or robotic systems. This is presently not possible due to a few key issues, one of which is actuation. The nature of D&D tasks requires the use of machines that have high payload to weight ratios. The machines in use today, which are based on conventional hydraulic actuation technology, have a payload to weight ratio of approximately 2 lb/lb. In comparison, manipulation systems utilizing electric actuation have ratios below 0.35 lb/lb, providing the primary justification for hydraulic actuators. Unfortunately, there are many systemic problems associated with conventional hydraulic actuation systems. In general, hydraulic actuators are costly, have high maintenance rates, leak, are highly nonlinear and time varying in operation, and are highly energy inefficient. In particular, the poor controllability of these systems results in poor accuracy and sluggish response. Operators can compensate for some of these performance limitations, but a fundamental change is necessary to enable transitioning from teleoperated to fully autonomous systems. This proposal addresses an enabling technology that will allow much greater throughputs (an order-of-magnitude) by allowing automation of time consuming remote D&D tasks. The enabling technology is a new type of hybrid electric/hydraulic actuator.

## **Annual Progress Reports**

### **2002 Progress Report**

# Environmental Management Science Program Research in Pennsylvania

## Carnegie Mellon University

### 82873 – Design and Sensor-Based Control for Hyper-Redundant Mechanisms

**Principal Investigator:** Howie Choset

**Problem Area:** Deactivation and Decommissioning

Toxic materials in DOE sites pose a significant threat to DOE personnel who must inspect these locations. Working in confined spaces further complicates the situation especially when the workers must wear heavy and cumbersome protective suits. In many situations, a structure must be disassembled for proper inspection, which is costly and time consuming; this procedure is especially dangerous if structure is highly convoluted and contains unknown, and possibly hazardous, materials. A robot or conventional mechanism can clearly bypass the danger and perhaps expedite the characterization process because the person is removed from the site; moreover, the site and the person are not prepared (i.e., there is no need for special excavation or a protective suit). Conventional robots, however, are not suitable for these inspection tasks because they are not flexible enough to pass through and into target DOE inspection sites. The proposed work seeks to develop an articulated probe, called a *hyper-redundant mechanism*, which is a snake-like device that can exploit its many internal degrees of freedom to thread through tightly packed volumes transmitting images and data from remote locations inaccessible to conventional robots and people. These images will be used to form a virtual presence to the remote user.

The use of hyper-redundant mechanisms expedites the inspection process of tanks and structures in two ways: First, the inspection site does not require extensive set-up (e.g., sites do not have to be excavated) because the hyper-redundant robot can slither to virtually any entrance location. Second, the hyper-redundant robot can maneuver through the interior of tanks and highly convoluted structures “seeing” every nook and cranny of the interior without adding extra entrance ports or even partially taking the structure apart. These robots have the added feature that they are minimally invasive; in other words, they can travel through highly convoluted structures returning images to a remote location without disturbing the site. This is especially important in aging tanks where the condition of the internals is completely unknown.

The many degrees of freedom that furnish a hyper-redundant mechanism its wide range of capabilities also provide its major challenges: mechanism design, path planning/control, and sensor integration, all of which are addressed by the proposed effort. Thus far, virtually all previous hyper-redundant work was limited to mechanism development in the plane and the few three-dimensional robots were weak and flimsy. Our design provides a compact and strong device. Finally, unlike all prior work, we will develop control algorithms to direct the robot to navigate unknown three-dimensional spaces. Again, the challenge here is to coordinate all of the internal degrees of freedom to allow for purposeful motion.

## Annual Progress Reports

### 2002 Progress Report



## **Environmental Management Science Program Research in New York**

### **New York University of Medicine**

#### **59882 – Measurements of Radon, Thoron, Isotopic Uranium and Thorium to Determine Occupational and Environmental Exposure at Fernald Feed Materials Production Center**

**Principal Investigator:** Dr. Naomi H. Harley

**Problem Area:** Health/Ecology/Risk

The research at the Fernald Environmental Restoration Management Corporation (FERMCO) site will provide radionuclide data, and realistic risk evaluation for isotopic radon, thorium, uranium and lead exposure.

We have developed and tested a passive radon monitor with proven accuracy and precision that can be miniaturized to provide accurate personal exposure during remediation. These monitors will be used in areas and personal exposure assessment.

We have a novel aerosol particle sampler that can provide measurements of the particle size distribution over long time periods (days to weeks). This will be the first remediation to provide personal and area particle size distribution measurements. The aerosol particle size is the major determinant in lung dose variability.

There was historic occupational and environmental exposure to  $^{222}\text{Rn}$ . There will be exposure to  $^{228,226}\text{Ra}$ ,  $^{220,222}\text{Rn}$ ,  $^{228,230,232}\text{Th}$ , and  $^{210}\text{Pb}$  during remediation. There are 2 silos containing 4000 Ci of  $^{226}\text{Ra}$  which will undergo some form of vitrification. There are 8 waste pits containing radium, thorium and lead in particulate form with concentrations to 4000 pCi/g. These particulates will be airborne as material is resuspended during the excavation procedures. Our study will provide accurate personal exposure assessment for all of the hazardous procedures with data available throughout each process so that rapid decisions concerning risk can be made. On site and remote soil, water and air samples will provide a full delineation of the environmental radionuclide contamination. A realistic carcinogenic risk assessment, based on these extensive environmental and occupational measurements, will be available throughout the restoration.

### **Annual Progress Reports**

**1998 Progress Report**

**1999 Progress Report**

**2000 Progress Report**

# Environmental Management Science Program Research in New Mexico

## Lovelace Biomedical & Environmental Research Institute

### 59918 – Improved Radiation Dosimetry/Risk Estimates to Facilitate Environmental Management of Plutonium Contaminated Sites

**Principal Investigator:** Dr. Bobby R. Scott

**Problem Area:** Health/Ecology/Risk

The Office of Environmental Management is the custodian of large quantities of toxic radioactive materials from manufacturing and processing facilities after the United States halted nuclear weapons production. Because these materials include high-specific activity (HSA) and low-specific activity (LSA) alpha-emitting ( $\alpha$ E) isotopes of plutonium (Pu), DOE workers and the public can be at risk for inhaling airborne  $\alpha$ E particles. Examples of HSA- $\alpha$ E particles are particles of  $^{236}\text{PuO}_2$ ,  $^{238}\text{PuO}_2$ , and  $^{240}\text{PuO}_2$ . Examples of LSA- $\alpha$ E Pu particles are particles of  $^{239}\text{PuO}_2$ ,  $^{242}\text{PuO}_2$ , and  $^{244}\text{PuO}_2$ . It is generally not recognized that airborne HSA- $\alpha$ E particles or mixtures of HSA- $\alpha$ E and LSA- $\alpha$ E particles present special problems for evaluating health-effects risks for workers involved in decontamination, decommissioning, and remediation. These problems arise because inadequate dosimetry models are used for characterizing the intake by inhalation of airborne HSA- $\alpha$ E particles and the associated local internal radiation doses. This inadequacy is especially unfortunate for those who may be at risk of inhaling HSA- $\alpha$ E particles when their airborne concentration is very low (much less than one particle per cubic meter of air). Such exposures are considered to be in the stochastic-exposure paradigm. For this paradigm, one cannot say whether anyone will inhale an HSA- $\alpha$ E particle. However, should an individual inhale even one HSA- $\alpha$ E particle, the radioactivity intake can exceed the annual limit for nuclear worker exposure (annual limit on intake). One HSA- $\alpha$ E particle could therefore represent a relatively large intake of radioactivity. Furthermore, HSA- $\alpha$ E particles are unstable due to the alpha-decay energy absorbed within the particle. If the particle is deposited in the respiratory tract, it can subsequently fragment into smaller particles leading to more surface area available for particle dissolution. Thus, radioactivity moves more rapidly from the respiratory tract to the liver and skeleton, via the blood, than occurs for LSA- $\alpha$ E particles. However, because no existing dosimetry model is adequate for evaluating possible radiation doses from inhalation of airborne  $\alpha$ E particles for the stochastic-exposure paradigm, health risks from such exposures cannot be reliably evaluated. For these exposures to airborne  $\alpha$ E particles and for the stochastic-exposure paradigm, it is preferable to evaluate the distribution of possible cancer risks rather than evaluating the risk associated with the expected intake of radioactivity because risk estimates based on expected intake can lead to wasting millions and possibly even more dollars on excessive cleanup of residual radioactivity. This project will apply fundamental knowledge of mechanisms of cancer induction, aerosol physics, and radiation dosimetry to: (1) evaluate  $\alpha$ E particle inhalation/deposition probabilities for adult male and female workers and for different members of the public (children, teenagers, and adults of both sexes); (2) characterize HSA- $\alpha$ E particle breakup and its impact on translocation of radioactivity from the lung to the liver and skeleton; (3) evaluate deposition of  $\alpha$  energy in biological tissues for stationary and moving  $\alpha$ E particles; and (4) evaluate the distribution of possible doses to lung (local doses), bone (organ dose), and liver (organ dose) and associated cancer-risk distributions for specific  $\alpha$ E particle exposure scenarios relevant to environmental management of sites contaminated with  $\alpha$ E sources. The main product of this research will be a stochastic respiratory tract dosimetry/risk computer model for evaluating absorbed dose distributions and the associated health risks distributions. The research will contribute to building a stronger scientific basis for environmental management of Pu-contaminated sites and to substantially reducing cleanup costs for such sites by eliminating the need to evaluate health risks for the stochastic exposure paradigm based on the expected intake of radioactivity.



## **Annual Progress Reports**

**1998 Progress Report**

**1999 Progress Report**

**2000 Progress Report**

## **Environmental Management Science Program Research in Tennessee**

### **Oak Ridge National Laboratory**

#### **60218 – Novel Mass Spectrometry Mutation Screening for Contaminant Impact Analysis**

**Principal Investigator:** Dr. Chung H. Chen

**Problem Area:** Health/Ecology/Risk

This research addresses the DNA mutation due to the exposure to contaminated media and to promote a better understanding of the relationship between exposure and health impact which are among the top priorities in the Environmental Management Science Program (EMSP). The capability of rapid mutation screening is essential for sound risk analysis for various contamination sites. However, rapid DNA mutation screening technology is still not available. Our objective is to develop innovative mass spectrometry technology to achieve fast mutation screening from contaminated area and to reveal the linkage between gene mutation and contaminants. Mass spectrometry has the potential to achieve very fast speed sample analysis. However, the poor mass resolution and low detection efficiency for long DNAs limit the broad application for mutation screening. In this program, new innovative approaches for improving mass resolution and detection sensitivity will be pursued to achieve rapid DNA screening. Allele specific polymerase chain reaction (ASPCR) will be coupled with the proposed novel mass spectrometry for detecting DNA mutations. At completion of the technology development, the merit of our approach will be directly tested by analyzing the possible mutations in ras gene wildlife, such as fish, exposed to environmental genotoxic agents. Successful accomplishment of the program will allow that genotoxic effect of hazardous waste to be routinely assessed directly at DNA level at an affordable cost.

### **Annual Progress Reports**

**1998 Progress Report**

**1999 Progress Report**

**2000 Progress Report**

# **Environmental Management Science Program Research in Georgia**

## **Georgia Institute of Technology**

### **60474 – Ultrahigh Sensitivity Heavy Noble Gas Detectors for Long-Term Monitoring and Monitoring Air**

**Principal Investigator:** Dr. John D. Valentine

**Problem Area:** Health/Ecology/Risk

A Georgia Institute of Technology/Argonne National Laboratory team will develop and demonstrate novel ultrahigh sensitivity heavy noble gas (krypton, xenon, and radon) detectors for long-term monitoring of spent fuel and TRU waste, as well as for distinguishing background radon alpha particles from other alpha emissions in air monitors. A new technique for concentrating the heavy noble gases from air will be integrated with state-of-the-art radiation detector technology to provide sensitivities on the order of two orders of magnitude better than current technology. In addition, these detectors can be configured such that heavy noble gas concentration in air is monitored continuously and recorded in real-time and in situ. This real-time data acquisition coupled with the ability to measure the beta particles and gamma rays emitted by krypton and xenon in coincidence mode will result in an enhanced ability both to use spectral information to detect and identify the different noble gas isotopes and to discriminate against all other signals. Finally, such an integrated concentration and detection system has the potential to provide low-cost and low-complexity detectors which would be ideally suited for long-term monitoring and fieldable air monitors.

It is proposed that a broad range of potential detectors and measurement techniques be identified and evaluated for use in DOE Environmental Management applications. Furthermore, at least two of the most promising techniques for detecting the heavy noble gas emissions will be developed experimentally. First, the concentrated radioactive gases can be mixed directly with standard proportional detector filled gases such that a 100% detection efficiency is realized when the mixture is passed through a proportional detector. Second, the concentrated gases can be used in scintillator flow-cell geometry to achieve a similar detection efficiency. While both of these techniques provide the ability to distinguish alpha and beta particle interactions within the detector, a gamma-ray spectroscopy detector can be used in coincidence mode with both techniques to further enhance background discrimination and species identification. Consequently, coincidence mode operation will also be demonstrated experimentally using both the proportional and the flow-cell detectors. If additional detectors and techniques are identified as promising, similar experimental development will be pursued for those systems. Finally, the developed detection systems will be evaluated and one or more systems identified, constructed, and demonstrated. This final demonstration of the technology will be conducted initially in the laboratory environment to establish operating characteristics, and subsequently will be conducted at a DOE EM site. To complete this detector development, a three-year team effort is proposed.

## **Annual Progress Reports**

**1998 Progress Report**

**1999 Progress Report**

**2000 Progress Report**

# **Environmental Management Science Program Research in California**

## **University of California at Irvine**

### **69848 – Adaptive Response Against Spontaneous Neoplastic Transformation in vitro Induced by Ionizing Radiation**

**Principal Investigator:** Dr. J. Leslie Redpath

**Problem Area:** Health/Ecology/Risk

The following paragraphs outline a project which addresses the area “Understanding biological responses to radiation and endogeneous damage”. The proposed research addresses the following key question: (a) “How much do low doses of radiation protect against subsequent low doses of ionizing radiation?”. The experimental system to be employed to address this question is the HeLa x skin fibroblast human hybrid cell system with which the investigators have over 12 years of experience and, importantly, with which they have made several observations which can be expended upon to address the question posed above. The endpoint to be employed is neoplastic transformation frequency. Two radiation sources will be used. These are Cs-137 gamma rays (0.66 MeV gamma energy) and 80 kVp X-rays used in fluoroscopy. While these two energies of photons are in what is normally considered the low LET range (0.4 to 5.0 keV/u), they do have a difference in biological effectiveness of perhaps a factor of 2. Notice 99-14 specifically notes the need to quantify the generality and extent of the apparent adaptive response in cells irradiated with small doses of radiation. This is the focus of the proposed effort. Total doses to be used, whether single or fractionated, will be no more than 10 cGy. Appropriate attention is given to the necessity for accurate dosimetry. The experimental protocol is designed such that the data obtained will be amenable to the rigorous statistical analysis so essential to evaluate low dose effects. The investigators have already demonstrated that irradiation with a single dose of 1 cGy results in a neoplastic transformation frequency that is a factor of two LOWER than that of sham-irradiated cells. It is proposed to expand on this observation by establishing a dose-response relationship (e.g. 0.1, 1.0 and 10.0 cGy) as well for repeated low dose exposures (e.g. 10 x 0.1 cGy and 10 x 1 cGy). These proposed experiments directly address the question posed in Notice 99-14. Transformation frequencies will be compared to those predicted by linear extrapolation of high dose data (2 and 4 Gy) through the spontaneous background frequency. This will provide an estimate of the factor by which such linear extrapolations can overestimate low dose data. It is also proposed to take advantage of another observation in the investigators laboratory to address, albeit indirectly, the question of the role of repair in this response. The investigators have previously shown that post-irradiation holding at room temperature prior to plating for focus formation results in enhanced cell kill and enhanced neoplastic transformation, most likely through the promotion of misrepair. It is now hypothesized that if the adaptive response involves the induction of a repair process then the reduction in transformation frequency following exposure to 1 cGy would be abrogated by post-irradiation holding at room temperature.

## **Annual Progress Reports**

### **2000 Progress Report**

### **2001 Progress Report**

# Environmental Management Science Program Research in Georgia

## Medical College of Georgia, Institute of Molecular Medicine and Genetics

### 69906 – Markers of the Low-Dose Radiation Response

**Principal Investigator:** Dr. William S. Dynan

**Problem Area:** Health/Ecology/Risk

Ionizing radiation has a unique ability to induce damage simultaneously at multiple sites within a spatially restricted region of DNA. The resulting double-strand DNA breaks (DSBs) present a major threat to the integrity and stability of the genome. Our understanding of the origin and fate of DSBs is based primarily on studies at high radiation doses. Despite recent progress toward the elucidation of molecular mechanisms underlying DSB repair, technologies are still not available to visualize individual DSB and DSB repair complexes in situ, in irradiated cells. This problem is particularly acute at low doses and low dose rates, where it is not currently possible to measure small numbers of DSBs against a large background of undamaged DNA and uninjured cells.

The goal of this work is to develop a technology that will allow direct in situ visualization of DSB repair complexes. These studies will help bridge the gap between biochemical studies of repair enzymes and an understanding of the process of repair as it actually occurs within the radiation-injured cell. Evidence suggests that DSB repair is a spatially organized process that takes place within self-assembling subnuclear structures. Previous knowledge of the biochemistry of DSB repair will facilitate the development of reagents that bind selectively to the active, assembled form of DSB repair proteins. These reagents will then be used to visualize DSB repair complexes in situ and to perform quantitative studies of the biological response to low dose radiation. This interdisciplinary effort will bring together specialists in molecular biology, radiobiology, and imaging technology.

#### **Specific goals of the research include:**

The development of tools for in situ visualization of DSB repair complexes. These will include fluorescently tagged repair proteins that can be used to visualize complex assembly in living cells. They will also include recombinant single-chain antibodies (scFvs) that will be used to detect changes in the conformation and phosphorylation state of DSB repair proteins that accompany the assembly of the repair complex.

The use of these tools in combination with fluorescence microscopy to detect and characterize visible subnuclear structures associated with DSB repair. Various control and reconstruction experiments will be performed to correlate visible structures with biochemically-defined repair complexes. Strategies will be developed to prolong the lifetime of repair complexes to make them more easily visible. Immunoprecipitation experiments will be performed to identify additional proteins that contribute to formation of repair structures.

A demonstration of the practical utility of the tools and assays developed in RESEARCH GOALS 1 and 2 by quantitative studies of DSB repair in different cell types. The formation of repair complexes at high and low radiation doses will be compared. The effect of a low radiation dose on the response to subsequent, higher, doses will be determined. The relative prevalence of the Ku-dependent end joining and Rad51-dependent recombinational pathways will be investigated.

The ability to visualize single DSB repair complexes formed at the sites of DNA damage will provide an improvement of two orders of magnitude in sensitivity over existing physical methods of measuring double-strand breaks. It will open up exciting prospects for direct investigation of the low-dose radiation response.

## **Annual Progress Reports**

**2000 Progress Report**

**2001 Progress Report**

# **Environmental Management Science Program Research in New Mexico**

## **Los Alamos National Laboratory**

### **69938 – Biological Effects of LLIR and Normal Oxidative Damage: The Same or Different?**

**Principal Investigator:** Dr. Edwin H. Goodwin

**Problem Area:** Health/Ecology/Risk

We propose to establish an oxidative stress laboratory where experiments can be conducted on cells grown in gas mixtures containing from 2.5 to 95% O<sub>2</sub>. This 38-fold difference will result in dissolved O<sub>2</sub> concentrations ranging from slightly hypoxic, to physiological (4.3% O<sub>2</sub> at the elevation of Los Alamos), through “normal” atmospheric cell culture conditions (19% O<sub>2</sub>) to clearly hyperoxic. Taking the physiological O<sub>2</sub> concentration as the appropriate control condition, we will examine and compare the consequences of inducing genetic damage either by low-level ionizing radiation (LLIR) or temporary exposure to elevated O<sub>2</sub>. We will determine if transient oxidative stress induces the same genetic effects, such as DNA base damage, chromosome aberrations, HPRT mutation, and transformation, as exposure to ionizing radiation. Furthermore, we will determine if important cellular responses, such as bystander effects, the adaptive response, and genomic instability can be induced by LLIR without the additional oxidative stress imposed by atmospheric O<sub>2</sub>, or if the threshold dose for initiating these effects changes.

## **Annual Progress Report**

### **2000 Progress Report**

# **Environmental Management Science Program Research in Washington**

## **Pacific Northwest National Laboratory**

### **69939 – Sensitivity to Radiation-Induced Cancer in Hemochromatosis**

**Principal Investigator:** Dr. Richard J. Bull

**Problem Area:** Health/Ecology/Risk

Determination of dose-response relationships for radiation-induced cancer in segments of the population with high susceptibility is critical for understanding the risks of low dose and low dose rates to humans. Clean-up levels for radionuclides will depend upon the fraction of the population represented by these people and the lower bounds on their sensitivity to radiation. Most research on susceptibility to radiation has focused on variations in DNA repair genes. However, important segments of the population with conditions that provide a differential growth advantage for mutated cells have not been examined. The long-term objective of this project is to indicate whether people with hereditary hemochromatosis (HH) would display an increased susceptibility to cancer induced by low LET radiation. We propose to pursue this question experimentally with mice having the same mutation as that found in the human disease, HFE knockout mice (Zhou et al., 1998). It is postulated that the major impact of HH will produce a “promotional” environment for radiation-induced cancer. In part this may be attributable to an increased likelihood of developing non-insulin-dependent diabetes mellitus (NIDDM). Development of NIDDM can be influenced by iron overload, but appears to be also found in heterozygotes where iron load is not an obvious factor (Nelson et al., 1995). If the HFE-knockouts are found to have higher sensitivity to radiation than their wild-type counterparts, steep dose response curves are anticipated that can serve to more clearly identify non-linearity or thresholds in the dose-response curve for low LET radiation. A pilot study using HFE-knockout homozygotes and heterozygotes has been designed to: 1) determine whether the knock-out mice have greater sensitivity to radiation-induced cancer of the colon, liver, and breast, 2) establish the dependence of this sensitivity on accumulation of iron, 3) determine the extent to which cell replication and apoptosis occur in these target tissues with varying iron load, and 4) correlate the increases in sensitivity with changes in insulin-related signaling in tumors and normal tissue from each target organ.

### **Annual Progress Report**

#### **2000 Progress Report**



# **Environmental Management Science Program Research in Washington**

## **Pacific Northwest National Laboratory**

### **69941 – Linking Molecular Event to Cellular Responses at Low Dose Exposures**

**Principal Investigator:** Dr. Jeffrey D. Saffer

**Problem Area:** Health/Ecology/Risk

Defining low dose radiation cancer risks is limited by our ability to measure and directly correlate relevant cellular and molecular responses occurring at low dose and dose rate with tumor formation. This deficiency has led to conservative risk assessments based on low dose extrapolation models. A model system that would allow a direct correlation between observable cellular and molecular responses required for cellular transformation, and how these responses are modulated by low dose radiation, could provide a scientific basis to improve current risk assessments. We have now defined a cell transformation system in which there is a clear inhibitory effect of low dose (2 rad) gamma radiation on cell transformation. We also have the molecular foundation to permit investigation of thresholds in molecular and cellular responses. The proposed work will obtain a quantitative understanding of the underlying mechanisms and their relationship to clonal expansion in order to establish the principles for low dose responses and to provide the data necessary for modeling effects below experimentally detectable limits. Establishing thresholds for critical regulatory steps in transformation-related signal transduction pathways would be an important advancement in the risk assessment of low dose radiation. These thresholds could be used to demonstrate non-linear relationships between low dose radiation and clonal expansion. If these data are appropriately incorporated into risk assessment models they could dramatically impact clean up levels and calculated risks to workers. This should ultimately reduce the cost of cleaning up contaminated DOE sites.

The system of choice for these studies is the mouse JB6 model. This is the best characterized system for linking cell signaling responses to clonal expansion, providing established connections between cell signaling pathways and clonal growth, as well as a broad range of genetic tools for exploring low dose responses. The work proposed will:

Define the effect of low dose radiation on EGF- and TPA-mediated transformation in JB6 cells.

Determine whether molecular events (ERK activity, AP-1, p107) known to be critical for transformation exhibit thresholds that are perturbed by low-dose radiation.

Determine whether low dose radiation modulates the course of oxidative stress required for cellular transformation in response to tumor promoters.

Determine whether the low dose radiation response demonstrated *in vitro* are relevant to *in vivo* processes using a standard mouse skin initiation-promotion strategy. To date, the molecular processes defined as critical for JB6 transformation that have been examined *in vivo* have shown a direct extrapolation.

## **Annual Progress Report**

### **2000 Progress Report**

# **Environmental Management Science Program Research in Middlesex, United Kingdom**

## **Gray Laboratory Cancer Research Trust, Mount Vernon Hospital**

### **69981 – Mechanisms of Enhanced Cell Killing at Low Doses: Implications for Radiation Risk**

**Principal Investigator:** Dr. Michael Joiner

**Problem Area:** Health/Ecology/Risk

We have determined previously that radiation sensitivity can be dose-dependent so that small acute exposures (and possibly exposures at very low dose rates) are more lethal per unit dose than larger exposures above a threshold (typically 5-40 cGy) where radioresistance increases. We have termed these dual phenomena low-dose hypersensitivity (HRS) and increased radioresistance (IRR) as the dose increases. HRS/IRR has been recorded in cell-survival studies with yeast, bacteria, protozoa, algae, higher plant cells and insect cells. However, we were first to demonstrate this phenomenon in mammalian cells and over the past decade, we have accumulated data indicating that HRS/IRR is widespread in both immortalized and non-immortalized human cells *in vitro*, and in animal normal-tissue models *in vivo*. More recently, research has revealed this phenomenon in the epidermis of patients undergoing radiotherapy for prostate cancer. We therefore believe that HRS may be the constitutive response of all normal cell systems to low-dose radiation exposures, which contrasts with the belief held for many years.

Our overall aim in this project is to gather understanding of the mechanisms underlying HRS/IRR. Little is currently known. However, there is now some direct evidence that this dose-dependent radiosensitivity phenomenon reflects changes in the amount, rate or type of DNA repair, rather than indirect mechanisms such as modulation of cell-cycle progression, growth characteristics or apoptosis. There is also indirect evidence that cell survival-related HRS/IRR in response to single doses might be a manifestation of the same underlying mechanism that determines the well-known *adaptive response* in the two-dose case, thus HRS can be removed by prior irradiation with both high- and low-LET radiations as well as a variety of other stress-inducing agents such as hydrogen peroxide and chemotherapeutic agents. Changed expression of some genes, only in response to low and not high doses, may occur within a few hours of irradiation and this might be rapid enough to explain this.

Our goals in the project are therefore:

Identify which aspects of DNA repair (amount, rate and type) determine HRS/IRR.

Investigate the known link we have discovered between the extent of HRS/IRR and position in the cell cycle, focusing on changes in DNA structure and conformation which may modulate DNA repair.

Use the results from studies in (1) and (2) to distinguish, if necessary, between HRS/IRR and the *adaptive response*. The aim is to finally determine if these are separate or interlinked phenomena.

Use the results from studies in (1), (2) and (3) to propose a mechanism to explain HRS/IRR.

## **Annual Progress Reports**

### **2000 Progress Report**

### **2001 Progress Report**

# **Environmental Management Science Program Research in Tennessee**

## **Oak Ridge National Laboratory**

### **73807 – Rapid Nucleic Acid Analysis for Contaminant Evaluation**

**Principal Investigator:** Dr. C. H. Winston Chen

**Problem Area:** Health/Ecology/Risk

This proposal addresses the types of DNA mutations and messenger RNA (mRNA) variation which occur as a result of exposure to contaminated media. It is also to promote a better understanding of the relationship between exposure and health impact, which are among the top priorities in Environmental Management Science Program (EMSP). Rapid and inexpensive DNA and RNA screening is critically needed to obtain a database for evaluation. In addition, it is very desirable to have the capability to do mutation analysis in the field so that the cost and time for risk evaluation can be significantly reduced.

This proposal is to develop high throughput, inexpensive and reliable analysis of DNA mutation due to exposure to contaminants. It will also be applied to mRNA so that the impact of pollutants to gene expression can be evaluated. The emphasis will be placed on the monitoring the change due to the contaminant exposure. The specific approaches are (1) to develop innovative multiplexing hybridization detection for DNA mutation detection, (2) to develop sequence-proof microarray hybridization technology, (3) to develop a field use computer disk hybridization (CDH) device for *in situ* nucleic acid analysis and (4) to apply the proposed technologies for mutation analysis of contaminated fish and to validate the pollutant-mediated mutation can be used for sound risk analysis for setting up the priorities for waste cleanup.

## **Annual Progress Reports**

**2000 Progress Report**

**2001 Progress Report**

**2002 Progress Report**

# Environmental Management Science Program Research in New Mexico

## Lovelace Biomedical & Environmental Research Institute

### 73942 – Improved Radiation Dosimetry Risk Estimates to Facilitate Environmental Management of Plutonium Contaminated Sites

**Principal Investigator:** Dr. Bobby R. Scott

**Problem Area:** Health/Ecology/Risk

New data are emerging that relate to health effects in humans who inhaled relatively large amounts of Plutonium (Pu). These data relate to nuclear workers in Russia who participated in their nuclear weapons program from the late 1940's through the 1960's. Many of these workers inhaled large amounts of  $^{239,240}\text{PuO}_2/^{241}\text{Am}$ . With a recent change in policy in Russia toward sharing scientific information with the west, clinical data related to health effects induced by alpha radiation are now being published at a very fast rate. In addition, improving characterization of source terms for Pu exposure is now feasible via Monte Carlo methods. In this project, we will use the new health-effects data along with improved methods of characterizing soil resuspension/transport via air, receptor intake or Pu-contaminated dust, subsequent organ radiation doses, and associated health risks to develop an improved integrated risk-assessment capability. We will use the probability distribution approach to address variability/uncertainty. The improved integrated-risk-assessment capability will facilitate obtaining improved radionuclide soil action levels (RSALs) for sites such as Rocky Flats. RSALs based on inadequate analyses and/or compounding of overly conservative assumptions could lead to wasting millions or more dollars on cleanup of Pu-contaminated sites.

DOE workers involved in decontamination and decommissioning (D&D) activities sometimes work in 100% lethal air concentrations of Pu. However, the workers wear protective clothing and respirators. For dealing with  $\text{PuO}_2$  particle penetration through respirators to worker breathing zones, faulty respirator incidents, and possible accident situations, guidance is needed for respiratory selection and for procedures to carry out should an incident or accident occur (e.g., treatment, follow-up medical surveillance). For other toxic agents, the immediately dangerous to life and health (IDLH) concept has been used to develop worker protection schemes for work in toxic atmospheres. Some have proposed use of the IDHL concept for Pu atmospheres at DOE facilities that arise during D&D activities. However, the IDLH is inappropriate for  $\text{PuO}_2$  atmospheres that arise during D&D operations because lethal intakes of  $\text{PuO}_2$  could arise without posing an immediate danger to life and health. Use of the IDLH concept for  $\text{PuO}_2$  could lead to costly litigation against the DOE for negligence in protecting workers. Our research will provide an acceptable alternative to use of the IDLH concept in developing worker protection criteria for D&D operations in  $\text{PuO}_2$ -contaminated atmospheres. Unlike the IDLH approach, our approach will not invite litigation against the DOE.

The intake of high- and low-specific-activity  $\text{PuO}_2$  during D&D faulty respirator incidents and accidents can vary considerably (e.g., by more than an order of magnitude). The biological dosimetry capabilities to be developed in this project will help to characterize actual intake via inhalation of Pu by DOE workers during incidents/accidents and by members of the public during extended residence at a Pu-contaminated site.

The public could greatly benefit from easy access to additional information about radiation and radiation issues. This project would maintain a web site with well-communicated educational material specifically designed for the public. A public more educated about radiation and radiation issues would be a benefit, not only to DOE, but also to our nation.

## Objectives:

This project has the following six objectives:

1. To use new data from studies of Russians exposed by inhalation to Pu and standard and novel analytical methods to develop improved characterization of health risks to the public from inhaled PuO<sub>2</sub>-contaminated soil originating from pre- and post-remediated DOE sites,
2. To contribute significantly to improving the probabilistic approach for selecting RSALs for sites where soil is contaminated with Pu (e.g., Rocky Flats Environmental Technology Site),
3. To use new data from studies of Russians exposed to Pu and standard and novel analytical methods to develop improved characterization of health risks to DOE workers who inhaled airborne PuO<sub>2</sub> during D&D operations (including faulty respiratory incidents),
4. To design a reliable system of respirator protection for workers involved in D&D work for the DOE at Pu-contaminated facilities.
5. To develop improved biodosimetry capabilities for evaluating Pu intake based on clinical data for Russians who inhaled <sup>239,240</sup>PuO<sub>2</sub>/<sup>241</sup>Am
6. To continue to provide educational material about radiation and radiation issues to the public and others via the web.

## Annual Progress Report

### 2001 Progress Report

### 2002 Progress Report

## **Environmental Management Science Program Research in New York**

### **New York University of Medicine**

#### **74050 – Measurement of Radon, Thoron, Isotopic Uranium and Thorium to Determine Occupational and Environmental Exposure at USDOE Fernald**

**Principal Investigator:** Dr. Naomi H. Harley

**Problem Area:** Health/Ecology/Risk

The goal of this research is to determine the detailed spatial environmental concentration, dispersion, resuspension and personal exposure for radon, thoron and thorium isotopes during removal of radium from the silos and thorium-230 from the waste pits at Fernald.

EMSP was developed to facilitate rapid transfer of laboratory based research, to remediation of DOE sites, providing new procedures for site characterization, exposure assessment, dose and risk reduction, and to reduce the overall costs. Our EMSP project has produced 2 new instruments, one a miniature passive alpha track detector that measures both radon and thoron simultaneously for either personal or environmental distribution studies, and two, a miniature integrating particle size analyzer that runs unattended for up to several weeks to measure air concentration of alpha emitting particulates and their size distribution (spectrum).

Both instruments have been deployed at Fernald for about 1 year, thus complying with our obligation of rapid transfer of our research to the Fernald site, and providing data which otherwise would not have been obtained.

To accomplish the goals stated above, three tasks are to be completed in the renewal.

One, modifications to both instruments were suggested by site personnel at Fernald who now use our measurements for site characterization. The final design versions of both our miniature personal radon and thoron gas detector, and our particle size analyzer are in place waiting implementation.

Two, to use the radon thoron detector, and our particle size analyzer to provide detailed characterization of airborne radionuclides, i.e., a network or grid of samplers for modeling concentration, dispersion and transport of radon, thoron, and particles as well as detailed personal exposure assessment.

Three, to perform the radiochemical analyses of soil samples taken around the radium (K-65) silos before and after removal of the material. The samples taken before removal are in process. This task is performed by our radiochemist consultant at the USDOE EML. A fraction of the lead-210, the long lived decay product of radon, deposits on the soil following radon decay and provides a sensitive tracer to determine the entire inventory of radon released during removal of the K-65 radium.

The new instruments provide research quality data for modeling of radon dispersion around the silos before and during removal of radium (K-65). They locate the radon effect perimeter as well as providing personal exposure assessment of involved personnel. Two particle size samplers operate continuously and measure the radionuclide particulate concentration and its size distribution, mainly thorium-230, during waste pit excavation, in other areas at Fernald, and two locations in the New York, New Jersey area for QC background

In summary, the objective is to

- Produce the final versions of both the radon thoron personal detector and the particle size analyzer. The designs are completed and await implementation.
- Deploy the instruments in the existing and an expanded network around the silos and the waste pits to obtain data for modeling concentration, dispersion and exposure assessment.
- Use the data to determine the extent (perimeter) of influence of the radon release from the silos before and during radium removal, overall concentrations, and the agreement with existing models of gas dispersion.
- Use the particle size sample concentration and aerosol size data to determine air concentration, to model resuspension and transport of thorium-230 in the environment.
- Perform radiochemical analysis for the decay product lead-210 in soil samples around the silos before and after radium removal as a tracer for the radon inventory released (radiochemistry to be performed at USDOE EML, the “before” samples are in process).

## **Annual Progress Report**

### **2001 Progress Report**

### **2002 Progress Report**



## Environmental Management Science Program Research in Washington

### Pacific Northwest National Laboratory

#### 54621 – Chemical Speciation of Strontium, Americium, and Curium in High Level Waste: Predictive Modeling of Phase Partitioning During Tank Processing

**Principal Investigator:** Dr. Andrew R. Felmy

**Problem Area:** High-Level Waste

This proposal is to extend the work of an FY96 EMSP grant for examining the effects of organic chelate complexation of the speciation and solubility of Sr and trivalent actinides under strongly basic, high carbonate conditions, similar to those present in high-level waste tanks at U.S. Department of Energy storage sites. In the first three years of this research program a comprehensive experimental and modeling approach was implemented which focused on the displacement of Sr from organic chelators and the formation of important metal-chelate-hydroxide complexes for the trivalent actinides. This comprehensive approach involved coupled experimental solubility studies, spectroscopic measurements of solution speciation, molecular modeling studies which yielded information on species structure and energetics, and thermodynamic modeling efforts using the Pitzer thermodynamic model which is valid to high ionic strengths. Using this approach, research studies were completed on Sr and the trivalent actinide analog Eu(III) on four of the most important chelates in tank waste: EDTA, HEDTA, NTA, and IDA as well as on the important inorganic ligands, hydroxide and carbonate. All of these research results were published in the open literature. Although these studies have already proven useful in several waste tank applications, the complexity of many of the wastes, specifically with respect to ligand concentration and complexity of many of the wastes, specifically with respect to ligand concentration and competing metal content, shows that continued research is required in order to apply these results to a wide range of tank compositions.

Based upon our results, we proposed: 1) extension to important chelates not previously studied, 2) studies of competing metal ions, and 3) specific studies using Am(III)/Cm(III). The chelate complex studies will directly extend our previous research on EDTA, HEDTA, NTA, and IDA to citrate and oxalate. In addition, we propose to address the possible formation of mixed ligand-ligand complexes for Eu(III) in EDTA-HEDTA, EDTA-NTA, HEDTA-NTA, and chelate-carbonate solutions. The competing metal studies will address Ni, Al, Mn, and Fe. These studies will extend our previous work on the competing metal Ca. These fundamental data on chemical speciation and solubility will then be used to develop highly accurate thermodynamic models, which are valid to high ionic strength. Such thermodynamic models are widely used by scientists and engineers at Hanford and other DOE sites to help develop improved waste disposal technologies.



## **Annual Progress Reports**

**1997 Progress Report**

**1998 Progress Report**

**1999 Progress Report**

**2000 Progress Report**

# Environmental Management Science Program Research in Michigan

## The University of Michigan

### 54691 – Radiation Effects on Sorption and Mobilization of Radionuclides during Transport through the Geosphere

**Principal Investigator:** Dr. Lu-Min Wang

**Problem Area:** High-Level Waste

Successful, demonstrated containment of radionuclides in the near-field can greatly reduce the complexity of the performance assessment analysis of a geologic repository. The chemical durability of the waste form, the corrosion rate of the canister, and the physical and chemical integrity of the back-fill provide important barriers to the release of radionuclides. However, near-field containment of radionuclides depends critically on the behavior of these materials in a radiation field.

The principal sources of radiation in high-level nuclear waste are  $\beta$ -decay of the fission products (e.g.,  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$ ) and  $\alpha$ -decay of the actinide elements (e.g., U, Np, Pu, Am and Cm). Both types of radiation can cause important chemical and physical changes in materials (e.g., increase in leach rates, volume expansion, solid state radiolysis and bubble formation, and reduced cation exchange capacity). The radiation-solid interactions are complex because they involve a combination of ionization effects due to electronic excitations and ballistic effects due to elastic collisions. The strength of the radiation field decreases dramatically with time, and the type of radiation damage varies over time ( $\alpha$ -decay damage due to actinides dominates over  $\beta$ -decay effects due to fission products with increasing time due to the long half-lives of the actinides). Further, the radiation effects vary as a function of the type of solid (ionic vs. covalent), the type of damage (inelastic vs. elastic interactions), the temperature of the irradiation, and the kinetics of the annealing mechanisms.

We propose a systematic study of elastic and inelastic damage effects in materials in the near-field. These include: 1.) waste forms (glass and crystalline ceramics); 2.) alteration products of waste forms (clays and zeolites); 3.) back-fill materials (clays and zeolites). We have selected materials whose durability or chemical behavior can potentially have a major effect on the retention of radionuclides (e.g., monazite as a waste form; smectite clays in back-fill), *but* for which there is very little previous systematic study. We have not included canister materials in this research, as there is already a substantial body of previous work on radiation effects in metals.

The work draws on over twenty years of experience in studying radiation effects in minerals and complex ceramics and utilizes an unusual combination of studies of natural phases of great age with ion beam and electron irradiations of synthetic phases under carefully controlled conditions.

## Annual Progress Reports

[1997 Progress Report](#)

[1998 Progress Report](#)

[1999 Progress Report](#)

[2000 Progress Report](#)

# Environmental Management Science Program Research in California

## The University of California - Davis

### 54890 - Non-Invasive Diagnostics for Measuring Physical Properties and Processes in High Level Wastes

**Principal Investigator:** Dr. Robert L. Powell

**Problem Area:** High-Level Waste

The radioactive and mixed wastes currently stored in the 177 underground storage tanks at the Hanford Site of the U. S. Department of Energy are complex mixtures of insoluble sludge, soluble salts, and supernatant liquids. In most of the double-shell tanks, the insoluble sludge layer, comprised of densely packed and networked solid particles, exceeds one third of the total volume of waste. The slurries pumped from the tanks will require pretreatment steps to separate the waste into different categories (high level, low level, etc.) for appropriate disposal and treatment. It is planned to transport the waste to various processing plants, separation facilities, and among different storage tanks using cross-site transfer pipelines. The long-term remediation strategy calls for disposal of the high-level waste in deep geologic repositories in the form of vitrified glass.

The current perception is that high safety factors during transport can be maintained by diluting the waste slurries to obtain low viscosity mixtures. These can easily be transferred across the pipelines to the processing plants or other tanks. However, this option is not favored due to the high cost associated with separation of a higher volume of liquid from the mixture in the separation plants. Clearly, this is not a waste minimization strategy. Additional processing will be required for the diluent which itself can become a waste. In this case, waste minimization is directly related to the ability to transport the waste with little or no dilution under tightly controlled conditions. The need for careful evaluation of the waste transfer process via pipelines is recognized. Five of the six existing cross-site transfer lines between the 200 West and 200 East areas of Hanford Site have been plugged by the slurries. Replacement transfer pipelines are currently being constructed. New methodologies are being developed to reduce risk associated with equipment loss and plugging of the pipelines during transfer. One of the most important steps in defining these criteria is *property measurement and characterization* of the waste. The current plan is for off-line measurement of the properties of the waste. This process is expected to be time-consuming and extremely expensive over the lifetime of the project.

Elemental analysis of tank sludges reveal that the major insoluble components expected to be present are oxides and hydroxides of Al, Fe, Zr, and Cr, insoluble salts such as calcium phosphates, and aluminosilicate minerals. Transmission electron micrographs of some tank sediments show that nanoparticles of many phases are present, and they reveal that over 50% of the insoluble material in some of the tank sludges are smaller than 1  $\mu\text{m}$  and composed of colloidal particles. It has been shown that these particles form aggregates or clusters and that the size of the clusters depends on the particle composition, solution pH, ionic strength, concentration of solids, shear rate, and temperature. Further, it has been shown that suspension properties strongly depend on primary particle size, cluster size, and fractal dimension of the clusters. Given the strong dependence of the rheological properties on the environment under which the clusters exist, off-line measurements of the rheological properties have been under critical scrutiny. For example, once a sample is withdrawn from the process stream, its rheological (flow) properties will begin to change. Further, given that the material in the pipeline may not be homogeneous, it will be difficult to obtain a representative sample.

The proposed work seeks to directly address the need for a robust technique to provide a comprehensive characterization of the relevant rheological properties under actual processing conditions to permit the monitoring and control of transport tank slurries. The principal thrust is to address the issue of on-line viscosity measurement by examining two potential viable technologies, nuclear magnetic resonance

imaging (NMRI) and acoustic velocimetry. We focus on the fundamental scientific issues that must be overcome in order to implement these techniques. This effort consists of a collaboration between the University of California at Davis (UCD) and Battelle Pacific Northwest National Laboratory (PNNL). Each organization brings specific expertise to the project. UCD has a strong background in the application of NMRI to fluid mechanics while PNNL has the needed expertise in acoustic velocimetry. Further the collaboration assures that the focus on the tank retrieval and waste problems at the Hanford site will be maintained, as will the active consultation of engineers at the principal contractor at Hanford, presently, Westinghouse. In this regard, Dr. Harry Babad of Westinghouse Hanford Company has agreed to act as an advisor to the project. Dr. Babad is the science advisor to Dr. Susan J. Eberlein (manager of the Tank Waste Remediation Systems Technical Basis Group) and he is currently involved in the planning and guidance for the retrieval process, sluicing and waste transfer, of tank wastes.

## **Annual Progress Reports**

**1997 Progress Report**

**1998 Progress Report**

**2000 Progress Report**

# Environmental Management Science Program Research in Georgia

## School of Earth and Atmospheric Sciences

### **55042 – Quantify Silica Reactivity in Subsurface Environments: An Integrated Experimental Study of Quartz and Amorphous Silica to Establish a Baseline for Glass Durability**

**Principal Investigator:** Dr. Patricia M. Dove

**Problem Area:** High-Level Waste

An immediate goal of this OER/OEM initiative is the development of a predictive framework of kinetic data for mineral-solution reactions that accurately describes the current and future behavior of earth systems. Reaction rates and mechanisms are essential elements in deciphering mineral/material reactivity trends within compositional series or across a matrix of complex solution compositions. The goal of the research addresses this gap in our current understanding by quantifying the reactivity of crystalline and amorphous  $\text{SiO}_2$  phases in the complex fluids of natural systems.

There are a number of important motivations for quantifying  $\text{SiO}_2$  reactivity in the fluids of subsurface environments. First, quartz and silica glass are the compositional end-member crystalline and amorphous oxides to the large classes of silicate minerals and glasses. Second, an understanding of fundamental controls on the reactivity of simple  $\text{Si-O}$  bonded phases establishes baseline behavior for silica phases widely found in waste storage environments and the host rock silicate minerals. These minerals comprise >90% of the earth's crust and dominate virtually every repository rock-water system. Third, complex silicate glasses will be the front line of defense in containing radioactive wastes in both interim and long-term storage strategies. However, we have little quantitative understanding of pure  $\text{SiO}_2$  reactivity in the solutes of natural and perturbed groundwaters even though current EM strategy calls for dispersal of waste into silica-based glass materials.

Recent studies show that simple solutes, sodium and potassium significantly enhance the reactivity of silica minerals and that this salt effect has a complex pH-dependence. However, the effect of other solutes frequently found in groundwater and soil solutions in pristine or contaminated areas is poorly understood. Further, there is presently little quantitative knowledge of how reaction affinity modifies this solute dependence. Both of these issues are important because the available data suggest that solutes and reaction affinity exert complex rate enhancing as well as rate inhibiting effects. Given the experience and publication record of the P.I. in the geochemical kinetics of mineral-water interactions, the research is a cost-effective approach to advancing our basic and applied scientific knowledge of solute controls on silica reactivity in natural and engineered Earth Systems.

Using an experimental approach which integrates techniques from surface science and geochemical kinetics, this study will measure the dissolution rate of quartz and silica glass in a series of single and mixed solute solutions over a range of variable pH and temperature. Rates will be measured over a range of reaction affinities by adjusting the steady state silica concentration produced during the dissolution reactions. These data will allow us to construct a comprehensive quantitative model of solute controls on the reactivity of crystalline and glassy  $\text{SiO}_2$ . The kinetic portion of the study will be conducted in parallel with in situ and ex situ surface sensitive analyses of selected samples/conditions. Findings will establish quantitative relationships between silica reactivity and a number of solution chemistries which have never been investigated or are presently understood in only a qualitative sense. Further, they will allow us to test the hypothesis that the solvation properties of dissolved species govern silica reactivity in a systematic and predictable way. If valid, we may be able to develop a powerful predictive tool for accurately estimating the influence of complex solute chemistries found in subsurface environments on silica reactivity and durability.

## **Annual Progress Reports**

**1997 Progress Report**

**1998 Progress Report**

**1999 Progress Report**

# **Environmental Management Science Program Research in New York**

## **Syracuse University**

### **55179 – Acoustic Monitor for Liquid-Solid Slurries Measurements at Low Weight Fractions**

**Principal Investigator:** Dr. Lawrence L. Tavlarides

**Problem Area:** High-Level Waste

Treatment of the radioactive waste stored in tanks across the DOE complex will require real-time characterization and monitoring of the size and volume fraction of solids in slurries during retrieval, immobilization, and closure stages of waste processing. Acoustic probes have been shown to be quite effective in determining the solid content in solid-liquid suspensions. However, the presence of small amounts of gas present in the waste slurries formed, for example, by radiolytic degradation processes prevent the straightforward application of these probes to the waste slurries. The research will develop an acoustic probe for monitoring particle size and volume fraction in slurries both in the absence and the presence of gas bubbles. This will be accomplished by selecting the range of frequencies of acoustic waves for which the interference caused by the bubbles is minimal and by developing a theory for the acoustic wave propagation in solid-gas-liquid systems. The initial theoretical and experimental studies will be devoted to relatively well characterized three-phase systems to establish firmly the theory and the development of the probe. The latter studies will be devoted to more complex suspensions whose properties are similar to those encountered in various waste processes at the Hanford Site.

## **Annual Progress Reports**

[\*\*1997 Progress Report\*\*](#)

[\*\*1998 Progress Report\*\*](#)

[\*\*1999 Progress Report\*\*](#)

## **Environmental Management Science Program Research in Indiana**

### **University of Notre Dame**

#### **55229 – The NO<sub>x</sub> System in Homogeneous and Heterogeneous Nuclear Waste**

**Principal Investigator:** Dr. Dan Meisel

**Problem Area:** High-Level Waste

A collaborative program between ANL and PNNL is proposed to study the radiation, and radiation induced, chemistry of the NO<sub>x</sub> system in waste simulants. The study will develop a computer model providing predictive capabilities for future EM operations including the characterization and pretreatment efforts. Essentially all of the chemistry that takes place in underground storage tanks is initiated by the little understood radiolytic effects on the concentrated nitrite/nitrate systems and its interaction with organic components of the waste. The ANL effort will develop quantitative data base of the dynamics of the early processes following the deposition of energy in the waste. The PNNL effort will focus on the interaction of NO<sub>x</sub> with the organic components at slower time scales, and on identification of final products. The substrate systems will be complexants, paraffins, organic phosphates, phenylborates and their degradation products, all of which are of specific safety concern at various EM sites. The quantitative rate and yield data, and the mechanistic information from both efforts will be incorporated into a unified computer code that describes the chemical consequences of a variety of EM scenarios.

### **Annual Progress Reports**

[1998 Progress Report](#)

[2000 Progress Report](#)



## **Environmental Management Science Program Research in New York**

### **Brookhaven National Laboratory**

#### **59982 – Reactivity of Peroxynitrite: Implications for Hanford Waste Management and Remediation**

**Principal Investigator:** Dr. Sergie Lyman

**Problem Area:** High-Level Waste

Favorable conditions exist in Hanford solid and liquid waste for radiation-induced generation of peroxynitrite, a very powerful oxidizing and nitrating agent. A comprehensive series of fundamental studies is designed to provide mechanistic and quantitative appreciation of the contribution of peroxynitrite in the waste chemistry, which is presently not understood. These studies will include:

1. Determination of the radiochemical yields of peroxynitrite generated in chemical mixtures simulating the various phases (salt cake, slurry, supernatant) of radioactive waste;
2. Through mechanistic studies of metal- and CO<sub>2</sub>-catalyzed oxidations by peroxynitrite, estimation of the extent of peroxynitrite-mediated oxidative degradation of waste organic components;
3. Exploration of the feasibility of using controlled catalytic oxidation by peroxynitrite in remediation to destroy waste organic components, and to remove chromium from the waste sludges which would greatly increase waste compatibility with vitrification-based disposal technologies.

The results of these studies will contribute to better understanding of the radioactive waste chemistry and thereby to more informed decisions concerning disposals options and technologies.

### **Annual Progress Reports**

**1998 Progress Report**

**1999 Progress Report**

**2000 Progress Report**

# **Environmental Management Science Program Research in Pennsylvania**

## **The Pennsylvania State University**

### **60219 – Development of Advanced Electrochemical Emission Spectroscopy for Monitoring Corrosion in Simulated DOE Liquid Waste**

**Principal Investigator:** Dr. Digby MacDonald

**Problem Area:** High-Level Waste

The Department of Energy currently stores millions of gallons of high level liquid radioactive waste in underground, carbon steel-lined concrete tanks at the Hanford Reservation in the state of Washington and at the Savannah River Site in South Carolina. Because of the indefinite time of storage, general corrosion, even though it may occur only at a low rate, must be considered as a principal threat to tank integrity. However, various forms of localized corrosion (pitting, crevice corrosion, and stress corrosion cracking) are known to occur on iron and carbon steel in alkaline environments, in general, and on carbon steel in DOE liquid waste environments, in particular. Because localized corrosion often results in sudden and unexpected failures, knowledge of the conditions under which localized corrosion occurs is vital for assessing the possibility of failure and for assessing remaining life.

In this program, we propose to use a variety of electrochemical techniques, but most notably Electrochemical Emission Spectroscopy (EES), to explore the fundamental aspects of the general and localized corrosion behaviors of iron and carbon steel in alkaline environments, including stimulated DOE liquid waste. Our goal is to resolve important mechanistic issues using the most modern electrochemical and analytical techniques. These include the analysis of EES data in terms of non-linear dynamics methods; the use of Electrochemical Impedance Spectroscopy (EIS), rotating ring-disk voltammetry, chronoamperometry, and steady-state (dc) polarization techniques to explore the passive state of iron in these media; the determination of passivity breakdown potentials and induction times, as well as the characterization of electrochemical emissions due to metastable pitting; the analysis of electrochemical noise in the coupling current between a crack or a crevice and the external surfaces as a means of determining the mechanisms of these processes; and the further development of deterministic theories and models for predicting the evolution of corrosion damage. These studies are expected to resolve important mechanistic issues, including the origin of electrochemical emissions in general corrosion, the viability of current deterministic models and theories for describing the passive state and for predicting passivity breakdown and the nucleation of pitting, and the delineation of anodic dissolution and hydrogen-induced fracture as the mechanism of crack propagation in carbon steels in highly alkaline solutions. Although the principal emphasis will be on the fundamental aspects of the subject, we will also assess the potential of techniques developed in this work to be used for in-situ, continuous monitoring of corrosion in DOE's storage tanks.

The proposed, three-year research program will be carried out in The Pennsylvania State University's Center for Advanced Materials (CAM) under the direction of Prof. Digby D. MacDonald and Dr. George Engelhardt. Researchers in CAM have extensive experience in studying electrochemical and corrosion phenomena on metals and alloys under extreme environmental conditions, and many of the techniques developed in this previous work will be employed in the research program.

## **Annual Progress Reports**

**1998 Progress Report**

**1999 Progress Report**

**2000 Progress Report**

**2001 Progress Report**

# **Environmental Management Science Program Research in Tennessee**

## **Oak Ridge National Laboratory**

### **65328 – Electrically Driven Technologies for Radioactive Aerosol Abatement**

**Principal Investigator:** Dr. David W. DePaoli

**Problem Area:** High-Level Waste

The production of radioactive aerosols during treatment and retrieval operations in radioactive waste tanks presents a significant problem of cost, worker exposure, potential for release, and increased waste volume. As an example, conventional mist eliminators were not sufficient to treat off-gas in recent In-Tank Evaporation operations at Oak Ridge National Laboratory, resulting in contamination of system duct work and wetting and plugging of HEPA filters.

Electrically driven processes, including electrocoalescence, acoustic agglomeration, and electric filtration, are powerful means for improving aerosol elimination systems. Electrocoalescence and acoustic agglomeration work to increase the mean droplet size, a key to improving removal efficiency by conventional demisters. In addition, electric filtration provides the advantage of an additional controllable force over conventional approaches that depend on inertial forces for removal.

The proposed work is aimed at employing recent advances in theoretical approaches and experimental techniques to improve our understanding of how these processes may be employed most efficiently to aerosol problems. An integration of theoretical/numerical simulations and experimental measurement will be employed to accomplish the following particular goals:

- C Extend the current understanding of droplet interactions, and coalescence/agglomeration in both electric and acoustic fields to more general and realistic situations, including the effects of droplet surface charges, Brownian diffusion, ambient shear flow, and complexity inherent in real systems.
- C Extend the current understanding of electric filtration to include all known forces acting on droplets to develop a general predictive model of overall removal performance.
- C Investigate the capabilities of a novel approach to increase droplet coalescence-agglomeration in aerosol suspensions using a combination of acoustic and electric field effects. Through the coupling of these two fields it may be possible to significantly decrease the number concentration of aerosols and thus promote considerable easier separation.

These studies will serve to provide realistic measures of the capabilities of electrically driven means for enhanced aerosol removal. The fundamental understanding will provide the basis for development of innovative new approaches, and for optimizing removal processes. The developments made in this project could have a significant impact on many costly tank waste treatment operations.

## **Annual Progress Reports**

**1999 Progress Report**

**2000 Progress Report**

**2001 Progress Report**

# Environmental Management Science Program Research in Idaho

## University of Idaho

### 65351- Solution Effects on Cesium Complexation with Calixarene – Crown Ethers from Liquid to Supercritical Fluids

**Principal Investigator:** Dr. Chien M. Wai

**Problem Area:** High-Level Waste

Calixarene-crown ethers with rigid skeletons are superior to flexible crown ethers for separation of  $^{137}\text{Cs}$  from high level waste (HLW). However, this extraction methodology often requires undesirable solvents and the extraction efficiency is strongly dependent on the solvent polarity parameter. Recent research indicates that metal species can be extracted selectively using crown ethers or calixarenes dissolved in supercritical fluids. The advantages of using supercritical fluids such as  $\text{CO}_2$  as solvents for extraction of metals include: minimization of organic liquid wastes generation, ability to penetrate porous materials, and control of solvent strength by changing temperature and pressure. The solubility parameter of supercritical  $\text{CO}_2$  varies with density resembling that of liquid hexane at moderate pressures in the supercritical region to those of chlorinated solvents at very high pressures. Since the density of a supercritical fluid can be changed continuously by changing temperature and pressure, the variation of solvation behavior of a solute in the fluid phase may resemble that over a wide range of solvents. The main purpose of the proposed research is to study solvation effects on cesium complexation with calixarene-crown ethers from liquid to supercritical fluids as a function of density using spectroscopic methods including high pressure nuclear magnetic resonance (NMR). The cesium calixarene-crown ether systems are particularly interesting because the complex stability depends on stereochemical arrangement which can be measured by NMR. The supercritical fluid results will be compared with the spectroscopic data obtained from conventional solvent systems. The proposed research may lead to the development of a new solvent free method for selective removal of  $^{137}\text{Cs}$  from HLW. The information obtained from this study will also be useful for conventional solvent extraction applications with regard to solvent consideration and ligand design for effective separation of  $^{137}\text{Cs}$  from various aqueous solutions.

## Annual Progress Report

[1999 Progress Report](#)

[2002 Progress Report](#)

# Environmental Management Science Program Research in Washington

## Washington State University

### 65352 – Developing a Fundamental Basis for the Characterization, Separation, and Disposal of Plutonium and other Actinides in High Level Radioactive Waste: The Effect of Temperature and Electrolyte Concentrations on Actinide Speciation

**Principal Investigator:** Dr. Sue B. Clark

**Problem Area:** High-Level Waste

Currently, no fundamental basis exists upon which to describe or predict the chemical form, or speciation, of Pu and the other actinides in high level radioactive waste (HLW). Although DOE has supported research on Pu speciation in acidic systems as needed for separations processing during the Cold War, or in concentrated electrolytes to support Pu disposal in the Waste Isolation Pilot Plant (WIPP), application of the results from such programs to predict the speciation of Pu in HLW is not adequate. Chemical equilibria are dependent on system conditions. Conditions relevant to HLW include highly alkaline aqueous systems with extremes in electrolyte concentrations (e.g., 5 molal and greater), and elevated temperatures (e.g.,  $T = 300^{\circ}\text{C}$  is possible in the HLW repository). Consequently,

C characterizing Pu that is currently stored in the tanks must be done *ex situ* and is extremely expensive (in excess of \$1,000,000 per core extrusion),

C separating the non-radioactive components from the actinides and fission products in sludge to minimize HLW volumes is frequently not successful, and

C predicting the performance of a HLW repository for isolating the radioactivity from the human environment results in large uncertainties and very expensive, conservative engineering controls.

Clearly, the inability to anticipate the behavior of Pu and the other actinides in such systems is hampering DOE efforts to remediate the HLW tanks.

This proposal presents a plan to develop a scientific basis for describing the speciation of the actinides and Pu in such systems. This basis will consist of an experimentally-derived thermodynamic model of Pu/actinide complexation under chemically harsh conditions relevant to HLW. This project is a collaboration of chemists and geochemists from Washington State University (WSU), University of Idaho (UI), and Lawrence Berkeley National Laboratory (PNNL). This multi-disciplinary team represents established expertise in thermodynamics and actinide chemistry, and will provide training opportunities to students and post-doctoral associates.

We propose to systematically measure the effects of pH, electrolyte concentrations, and temperature on Pu and actinide solution chemistry in a  $\text{Na-NO}_3\text{-OH-H}_2\text{O}$  matrix. Both chemical analogs of the different oxidation states of Pu (e.g.,  $\text{Nd}^{3+}$ ,  $\text{Th}^{4+}$ ,  $\text{NpO}_2^{2+}$ , and  $\text{UO}_2^{2+}$ ) and Pu itself will be studied. We will determine the temperature dependence of ion interaction parameters for these cations with  $\text{NO}_3^-$ . Then, we will study their complexation behavior with  $\text{OH}^-$ , acetate, oxalate, and EDTA.

Our experimental plan combines several approaches intended to define the underlying molecular processes responsible for the electrolyte and temperature dependence of actinide complexation equilibria. Stability constants, enthalpies and entropies for complexation will be determined under alkaline conditions, and at variable ionic strengths and temperatures. In addition, spectroscopic tools will be used to directly observe changes in metal hydration for the complexes formed. Correlations between the temperature and ionic strength dependence of the primary hydration sphere and the observed stability constants will be used to elucidate the role of water in actinide complexation in such extreme conditions. Understanding the role of

water is an important parameter for developing a predictive model applicable to the myriad of possible actinide complexation reactions in HLW from a limited experimental data set.

Using the experimental results for the systems outlined above, we will build a Pitzer model to describe the speciation of Pu and the actinides in alkaline conditions as a function of elevated ionic strengths and temperatures. Our modeling efforts will be an extension of existing DOE research describing the temperature dependence of the electrolyte matrix for the Hanford waste tanks. We will add the “actinide specific” information to the temperature dependence Pitzer model for HLW. We will validate our model predictions by comparison to observed actinide and Pu speciation in actual HLW.

With the temperature dependence Pitzer model for Pu and the other actinides developed from this research program, DOE will be able to predict the speciation of Pu and the actinides over all ranges of temperatures and ionic strengths relevant to characterization, pretreatment and separation, and disposal of HLW. In addition, prediction of the conditions necessary to favor the formation of a desired chemical form will also be possible. With such a powerful predictive tool, the successful development of cost-effective technologies necessary to remediate the HLW tanks becomes much more probable.

## **Annual Progress Reports**

### **1999 Progress Report**

### **2000 Progress Report**

# **Environmental Management Science Program Research in Pennsylvania**

## **Pennsylvania State University**

### **65366 – Physical, Chemical and Structural Evolution of Zeolite-Containing Waste Forms Produced from Metakaolinite and Calcined HLW**

**Principal Investigator:** Dr. Michael Grutzeck

**Problem Area:** High-Level Waste

Natural and synthetic zeolites are extremely versatile materials. They can adsorb a variety of liquids and gasses, and also take part in cation exchange reactions. Zeolites are easy to make, they can be synthesized from a wide variety of natural and man made materials. One such combination is metakaolinite and sodium hydroxide solution. Our objective is to adapt this well known reaction for use in site remediation and clean-up of caustic waste solutions now in storage in tanks at Hanford and the Savannah River sites.

It has been established that a mixture of calcined equivalent ICPP waste (sodium aluminate/hydroxide solution containing 3:1 Na:Al) and fly ash and/or metakaolinite can be cured at various temperatures to produce a monolith containing Zeolite A (80°C) or Na-P1 plus hydroxysodalite (130°C) dispersed in an alkali aluminosilicate hydrate matrix. The zeolitization process is a simple one and as such could be a viable alternative for fixation of low activity waste (LAW) salts and calcines. Dissolution tests have shown these materials to have superior retention for alkali, alkaline earth and heavy metal ions.

The technology for synthesizing zeolites is well documented for pure starting materials, but relatively little is known about the process if metakaolinite is mixed with a complex mixture of oxides containing nearly every element in the periodic table. Zeolites have the ability to sequester ions in lattice positions or within their networks of channels and voids. As such they are nearly perfect waste forms, the zeolites can host alkali, alkaline earth and a variety of higher valence cations. In addition to zeolites, it has been found that the zeolites are accompanied by an alkali aluminosilicate hydrate matrix which is host not only to the zeolites but residual insoluble hydroxide phases as well. The purpose of the proposed work is to develop a clearer understanding of the advantages and limitations of producing a zeolite-containing waste form from calcined radioactive waste, i.e. the effect of processing variables, reaction kinetics, crystal and phase chemistry, and microstructure on their performance.

To accomplish this, it is proposed to simulate two waste forms representative of solutions in storage at the Hanford and Savannah River sites. Because nitrate is detrimental to the process, the LAW will be calcined at various temperatures (w/wo sugar) to maximize the reactivity of the resultant mix of oxide phases while minimizing the loss of volatiles. The oxides will be mixed with varying amounts and types of metakaolinite, small amounts of other chemicals (alkali hydroxides and/or carbonates, zeolite seeds, templating agents) and enough water to make a paste. The paste can then be cured (in-can) at a variety of temperatures (80°-100°C). Once reaction rates for the process are established, MAS NMR and TEM will be used to study the atomic-level structure of the solids. X-ray diffraction will be used to examine the degree of crystallinity of the waste forms. An environmental SEM will be used to track the development of microstructure in real time. An electron microprobe will be used to analyze the phases in the waste form. Attempts will be made to relate changes in phase chemistry and microstructure to distribution coefficients and dissolution data. Compressive and bending strength test will be used to determine mechanical behavior and standard leach tests will be used to determine the potential consequences of cation exchange reactions. Knowing that simulated waste is not an adequate predictor, a major portion of the proposed work will be carried out by Dr. Carol Jantzen at the Savannah River Technology Center; she will run parallel studies using actual LAW samples obtained from the Savannah River site. The value of running parallel studies of this type is self evident. Given these data, it is expected that it will be possible to piece together a coherent picture of how the crystal and phase evolution of an actual di-phasic zeolite-containing waste form made from LAW governs its performance and its durability once placed into service.



## **Annual Progress Reports**

**1999 Progress Report**

**2000 Progress Report**

**2001 Progress Report**

**2002 Progress Report**

# **Environmental Management Science Program Research in Washington**

## **Pacific Northwest National Laboratory**

### **65368 – Speciation, Dissolution, and Redox Reactions of Chromium Relevant to Pretreatment and Separation of High-Level Tank Wastes**

**Principal Investigator:** Dr. Dhanpat Rai

**Problem Area:** High-Level Waste

Chromium, one of the problematic constituents in tank sludges, is presently considered to be the most important constituent in defining the total volume of HLW glass to be produced from the Hanford tank wastes, because it greatly complicates the vitrification process by forming separate phases in the molten glass and, more importantly, current sludge washing processes are not effective in the removal of chromium from sludges could result in production of an unacceptably large volume of HLW glass.

The removal of Cr from tank sludges is complicated by factors including the complex chemistry of Cr, lack of fundamental data applicable to the HLW chemical systems (high heterogeneity, high ionic strength, high alkalinity and presence of inorganic and organic ligands, etc.), and the need to avoid processes that may adversely enhance the solubility of Pu and other actinides. Significant gaps exist in the fundamental understanding of Cr chemistry in tank-like environments. Without such understanding, these strategies cannot be appropriately evaluated or optimized.

We are taking an integrated approach of solubility measurements and spectroscopic characterization to study the speciation, dissolution and redox reactions of Cr under conditions relevant to HLW processing. Solubilities and dissolution rates of important Cr compounds are being determined as functions of ionic strength, alkalinity, redox conditions and temperature. Dominant Cr species in both solution and solid phases under these conditions will be characterized. A model describing the dissolution/precipitation behavior of Cr under HLW processing conditions will be developed and tested with controlled HLW sludge leaching tests.

The proposed study seeks fundamental knowledge of Cr chemistry in multicomponent, highly non-ideal electrolyte systems, providing critical data to support the development of pretreatment processes for the removal of Cr and thereby helping to achieve a major saving in the cost of HLW disposal at Department of Energy sites.

## **Annual Progress Reports**

**1999 Progress Report**

**2000 Progress Report**

# Environmental Management Science Program Research in Illinois

## Argonne National Laboratory

### 65378 – Complexants for Actinide Element Coordination and Immobilization

**Principal Investigator:** Dr. Mark R. Antonio

**Problem Area:** High-Level Waste

We propose that inorganic clusters known as polyoxoanions (POAs) can be exploited as complexants for actinide (*An*) ion coordination and immobilization. Our objective is to develop rugged, stoichiometrically well-defined POAs that act as molecular containers of *An* elements. Polyoxoanions are Group 6,  $d^0$  transition metal oxide clusters held together by metal-oxygen bonds. Molybdenum(VI) and tungsten(VI) form the largest number of POAs. In them, M-O polyhedra condense to form sturdy molecular aggregates with unprecedented conformational variability. Most are strong multielectron oxidants, and are soluble in both aqueous and organic media. By careful derivatization of POA metal-oxygen framework structures, selective and efficient *An* ion complexation should be achieved in alkaline and acidic high-level waste (HLW). Because POAs are metal-oxygen clusters, we envision that *An*-POA complexes should be readily immobilized in oxide waste forms. We propose to examine the thermochemistry of *An*-POA complexes under practical vitrification conditions. We will also determine the coordination and valence of *An* ions incorporated into oxide waste forms using *An*-POA precursors.

The application of POAs as inorganic complexants would offer benefits of cost effectiveness and environmental safety. They are commercially used as solid heterogeneous oxidation catalysts and homogeneous acid catalysts. The properties of POAs that make them suitable for catalysis (e.g., thermal stability, selectivity, reactivity, flexibility) make them attractive for their proposed dual-use in *An* ion complexation and tank waste immobilization. We will study solution and solid-state structures of *An*-POA complexes, their bonding, redox behaviors, and stabilities under practical tank conditions and under processing conditions relevant to HLW melts. The proposed work uses our expertise with the handling of actinides and POAs and the specialized actinide experimental facilities available at Argonne National Laboratory. These studies should ultimately aid in the rational design of inorganic, environmentally-benign, complexants for *An* ion immobilization.

## Annual Progress Reports

[1999 Progress Report](#)

[2000 Progress Report](#)

# **Environmental Management Science Program Research in Illinois**

## **Argonne National Laboratory**

### **65398 – Characterization of Actinides in Simulated Alkaline Tank Waste Sludges and Leach Solutions**

**Principal Investigator:** Dr. Kenneth L. Nash

**Problem Area:** High-Level Waste

The assumption that solubility of actinide ions will be low during alkaline sludge washing to remediate DOE's underground waste tanks is based on minimal experimental evidence, and the application of thermodynamic models of dubious validity to systems that may well be under kinetic control. The chemical speciation of actinides in actual waste tank sludges (oxidation states, actinide-bearing "mineral" phases, potentially soluble metal complexes) has not been reported in the peer-reviewed literature. The work described in this proposal is designed to provide new fundamental information on the chemical behavior and speciation of uranium, neptunium, plutonium, and americium in simulated alkaline tank waste sludges and alkaline scrub liquors. Sludges representative of those generated during plutonium production (BiPO<sub>4</sub>, REDOX, PUREX processes) will be prepared using appropriate combinations of chemical components of the various waste streams that contribute to the complexity of alkaline tank wastes. Actinide ions will be introduced in the oxidation states pertinent to process conditions at concentrations ranging from tracer level to macroscopic. Actinide speciation in the insoluble sludges will be examined using X-ray diffraction and other scattering techniques. Parallel studies will address the chemistry of actinide ions in alkaline solutions, principally those containing chelating agents. By correlating actinide speciation in the solid and solution phases with sludge composition, it will be possible to predict conditions that might favor mobilization of actinide ions during sludge washing. The new information will increase predictability of actinide behavior during waste tank remediation, and so contribute to minimization of the volume of high level waste created.

## **Annual Progress Reports**

**1999 Progress Report**

**2000 Progress Report**

# Environmental Management Science Program Research in Washington

## Pacific Northwest National Laboratory

### 65408 – Mechanisms and Kinetics of Organic Aging in High-Level Nuclear Wastes

**Principal Investigator:** Dr. Donald M. Camaioni

**Problem Area:** High-Level Waste

Uranium and plutonium production at the Hanford and Savannah River Sites produced nearly 100 million gallons of radioactive byproducts and contaminated process chemicals that are stored in underground tanks awaiting treatment and disposal. Scientific information is needed to support decisions and issue resolutions for safe, effective, and efficient waste storage and processing activities, including development of the Hanford Phase II privatization request for proposals. Tanks that contain organic process chemicals have many issues, including the following:

- The wastes can be at risk for fuel-nitrate deflagration accidents if allowed to dry out.
- The generation of flammable gases by organic-containing wastes is a major safety concern. Radiolytic and thermochemical processes degrade (“age”) organic solutes into smaller fragments of lower energy content, thereby reducing the hazard, while contributing to the generation of toxic, flammable and potentially explosive gases (i.e., volatile organic chemicals,  $\text{NH}_3$ ,  $\text{H}_2$ , and  $\text{N}_2\text{O}$ ).
- Aging of organic chemicals also produces toxic volatile organic vapors. Release of these vapors by the wastes causes concern for the health and safety of personnel working about the waste tanks.
- Changing waste storage conditions may alter organic aging to increase gas and organic vapor production. However, changes that accelerate aging of organic complexants also decrease the potential for combustion reactions and facilitate separation of radionuclides.
- Organic complexants in wastes interfere with radionuclide separation. Partitioning of radionuclides between the liquid and solid phases in the waste is hindered by organic complexants present in the wastes. The complexation of radionuclides must be controlled to separate the waste into high- and low-level fractions effectively. This may entail destroying the complexants or removing the dissolved radionuclides using advanced separation processes.
- Organic complexants modify the subsurface transport characteristics of wastes that have been disposed or leaked to the ground.

The goal of this project is to develop a fundamental understanding of organic aging and to assemble a model that describes and predicts the thermal and radiolytic aging of organic compounds in high-level wastes (HLW). To reach this goal, we will measure kinetics and elucidate products and mechanisms of organic reactions occurring under conditions of waste storage, retrieval, and processing. Initial emphasis will be placed on studying thermal effects, because organic reaction mechanisms and effects of varying conditions are uncertain, and because we benefit from collaborations with earlier Environmental Management Science Program (EMSP) projects that have worked on radiation effects. Organic complexants are of greatest concern regarding both safety and pretreatment because they have been found to degrade to gases, combust in dry wastes, and interfere with radionuclide separations. Therefore, efforts will focus on studying the reactions of these organic chemicals and associated degradation products.

In preliminary work, the authors have used mechanistic kinetic modeling techniques to successfully model the radiolytic degradation of formate to carbonate in HLW simulants. The research will continue development of the model using an iterative process that measures degradation products and kinetics of increasingly complex molecules while adapting the model to reproduce the results each step of the way. Experiments will elucidate mechanisms and kinetics of thermal degradations so that thermal and radiolytic

processes may be integrated within the model. Key kinetic data and thermodynamic properties relating to thermal reactivity will also be acquired so that rate-controlling and product-forming reactions can be predicted. Thermochemical properties of key intermediates will be experimentally and/or theoretically determined to facilitate mechanism verification, structure/reactivity correlation, and prediction of reaction rates.

We expect a comprehensive understanding of organic reactivity in HLW will accrue from the work. This understanding will be embodied in organic reaction models that predict distributions of species, including gases, with respect to time, temperature, and radiation history. These models will assist waste management decisions by predicting impacts of organic chemicals on safe storage, waste retrieval, and pretreatment of HLW.

## **Annual Progress Reports**

**1999 Progress Report**

**2001 Progress Report**

# **Environmental Management Science Program Research in Washington**

## **Pacific Northwest National Laboratory**

### **65409- Electroactive Materials for Anion Separation – Technetium from Nitrate**

**Principal Investigator:** Dr. Johanes H. Sukamto

**Problem Area:** High-Level Waste

The proposed research will provide the basis for using electroactive ion exchange materials to remove anionic contaminants from HLW wastes and process streams. An ion exchange process using electroactive materials sorbs contaminants selectively and then expels (elutes) them electrochemically by changing the charge balance through redox reactions in the sorbent as opposed to requiring the addition of a chemical eluant. Such processes can theoretically remove anions (e.g., pertechnetate, chromate) and concentrate them in a separate product stream while adding no process chemicals. A practical implementation in HLW process facilities would be a breakthrough in the ability of DOE to economically minimize waste and prevent pollution throughout the complex. To enable this, our work focuses on manipulating specific properties of redox polymers to control the hydrophobicity and ion-pair properties pertinent to the reversibility, selectivity, stability, intercalation/de-intercalation rates, and capacity of the polymers. This involves determining the density of charged sites, mobility of charged sites, degree of cross-linking, and polymer chain length. The work will be performed by: Pacific Northwest National Laboratory (synthesis and characterization of polymers); Brookhaven National Laboratory (direct characterization of ion-pair interactions); University of Minnesota (synthesis and characterization of high capacity polymers).

## **Annual Progress Reports**

**1999 Progress Report**

**2000 Progress Report**

# **Environmental Management Science Program Research in Washington**

## **Pacific Northwest National Laboratory**

### **65411 – Precipitation and Deposition of Aluminum-Containing Phases in Tank Wastes**

**Principal Investigator:** Dr. Jun Liu

**Problem Area:** High-Level Waste

Aluminum-containing phases represent the most prevalent solids that can appear or disappear during the processing of radioactive tanks wastes. Processes such as sludge washing and leaching are designed to dissolve Al-containing phases and, thereby, minimize the volume of high-level waste glass required to encapsulate radioactive sludges. Unfortunately, waste processing steps can involve solutions that are supersaturated with Al-species, resulting in unwanted precipitation or scale formation. Of all constituents of tank waste, Al-species have the greatest potential for clogging pipes and transfer lines, fouling highly radioactive components such as ion exchangers, and completely shutting down processing operations.

The primary focus of this proposal is to understand the major factors controlling precipitation, scale formation, and cementation of existing insoluble particles by Al-containing phases. Nucleation and growth phenomena will be studied using techniques including solid and liquid magnetic resonance techniques, small-angle x-ray scattering, transmission electron microscopy, and atomic force microscopy. Results will be used to predict and control precipitation, scale formation, and cementation under tank waste processing conditions. The results will also provide information regarding what Al-containing phases form and how soluble such phases are in basic tank waste solutions containing Na, Si, P, organics, and insoluble sludges. The project will have an important impact on waste minimization, and on the retrieval, transport and separation of tank wastes.

### **Annual Progress Reports**

**1999 Progress Report**

**2000 Progress Report**



# **Environmental Management Science Program Research in Massachusetts**

## **Massachusetts Institute of Technology**

### **65435 – Millimeter-Wave Measurements of High Level and Low Activity Glass Melts**

**Principal Investigator:** Dr. Paul P. Woskov

**Problem Area:** High-Level Waste

The objectives of the proposed multi-organizational research are to develop new real-time sensors for characterizing glass melts in high level waste (HLW) and low activity waste (LAW) melter, and to understand the scientific basis and bridge the gap between glass melt model data and melter performance. Millimeter-wave technology will be developed and applied to the simultaneous measurement of temperature, conductivity, and viscosity for the first time. Robust waveguide interfacing with the melter will make possible non-contact surface measurements, and internal melt measurements by waveguide immersion. Consequently, a significant advance is expected in the *in situ* capability and reliability of real-time monitoring of glass properties inside HLW and LAW melter. Laboratory studies will be undertaken over a wide range of waste glass chemistries to enable an understanding of the relationship between the melt chemistry and the millimeter-wave measurable characteristics. A basic goal is to characterize glass melts *in situ* with the new diagnostic capability so that data will represent the actual melt's behavior. The work will be closely coupled to the needs of the Defense Waste Processing Facility (DWPF), West Valley Demonstration Project (WVDP), and vitrification efforts at Hanford, Oak Ridge, and Idaho sites. The proposed sensors, when successfully developed, will decrease the uncertainty in current process control models and will allow for increases in waste loading. The proposed research will be a collaboration between the MIT Plasma Science and Fusion Center (PSFC), the Pacific Northwest National Laboratory (PNNL), and the Savannah River Technology Center (SRTC).

## **Annual Progress Reports**

**1999 Progress Report**

**2000 Progress Report**

# Environmental Management Science Program Research in Washington

## Pacific Northwest National Laboratory

### 73748 – New Metal Niobate and Silicotitanate Ion Exchangers: Development and Characterization

**Principal Investigator:** Yali Su

**Problem Area:** High-Level Waste

This renewal proposal outlines our current progress and future research plans for ion exchangers: novel metal niobate and silicotitanate ion exchangers and their ultimate deployment in the U.S. Department of Energy (DOE) complex. In our original study, several forms (including Cs exchanged) of heated treated Crystalline Silicotitanates (CSTs) were fully characterized by a combination of high-temperature synthesis and phase identification, low-temperature synthesis and phase identification, and thermodynamics. This renewal proposal is predicated on work completed in our current EMSP program: we have shown preliminary data of a novel class of niobate-based molecular sieves (Na/Nb/M/O, M=transition metals) that show exceptionally high selectivity for divalent cations under extreme conditions (acid solutions, competing cations) and novel silicotitanate phases that are also selective for divalent cations. Furthermore, these materials are easily converted by a high-temperature in situ heat treatment into a refractory ceramic waste form with low cation leachability. The new niobate-based waste form is a perovskite phase, which is also a major component of Synroc, a titanate ceramic waste form used for sequestration of high-level wastes (HLW) from reprocessed, spent nuclear fuel. These new niobate ion exchangers also showed orders of magnitude better selectivity for  $\text{Sr}^{2+}$  under acid conditions than any other material.

The goal of the program is to provide DOE with alternative materials that can exceed the performance of monosodium titanate (MST) for strontium and actinide removal at the Savannah River Site (SRS), remove strontium from acidic waste at Idaho National Engineering and Environmental Laboratory (INEEL), and sequester divalent cations from contaminated groundwater and soil plume. This program will provide DOE with materials for near-term, lab bench simulant testing and eventual deployment. The proposed work will provide information on the structure/property relationship between ion exchanger frameworks and selectivity for specific ions, allowing for the eventual “tuning” of framework for specific ion exchange needs. To date, DOE sites have become interested in onsite testing of these materials; ongoing discussions and initial experiments are occurring with Dr. Dean Peterman, INEEL (location of the DOE/EM West Treatment Focus Area) and Dr. John Harbour, SRS. Yet the materials have not been optimized, and further research and development of the novel ion exchangers and testing conditions with simulants are greatly needed. In addition, studies of the ion exchanger composition versus ion selectivity, ion exchange capacity, and durability of final waste form are needed.

This program will bring together three key institutions to address scientific hurdles of the separation process associated with metal niobate and silicotitanate ion exchangers, in particular for divalent cations (e.g.,  $\text{Sr}^{2+}$ ). The program involves a joint effort between researchers at Pacific Northwest National Laboratory, who are leaders in structure/property relationships in silicotitanates and in waste form development and performance assessment. Sandia National Laboratories, who discovered and developed crystalline silicotitanate ion exchangers, (with Texas A&M and UOP) and also the novel class of divalent metal niobate ion exchangers, and the Thermochemistry Facility at the University of California at Davis, who are world-renowned experts in calorimetry and have already performed extensive thermodynamic studies on silicotitanate materials. In addition, Dr. Rodney Ewing of the University of Michigan, an expert in radiation effects on materials, and Dr. Robert Roth of the National Institute of Standards and Technology (NIST) and The Viper Group, a leader in phase equilibria development, we will be consultants for radiation and phase studies. The research team will focus on three tasks that will provide both the basic research necessary for the development of highly selective ion exchange materials and also materials for short-term deployment within the DOE complex: 1) structure/property relationships of a novel class of niobate based molecular sieves (Na/Nb/M/O, M=transition metals), which show exceptionally high selectivity for

divalent cations under extreme conditions (acid solutions, competing cations); 2) the role of ion exchanger structure change (both niobates and silicotitanates) on the exchange capacity (for elements such as strontium and actinide-surrogates), which result from exposure to DOE complex waste simulants; 3) thermodynamic stability of metal niobates and silicotitanate ion exchangers.

## **Annual Progress Report**

### **2001 Progress Report**

### **2002 Progress Report**

# **Environmental Management Science Program Research in Washington**

## **Pacific Northwest National Laboratory**

### **73749 – Chemical Speciation of Strontium, Americium, and Curium in High Level Waste: Predictive Modeling of Phase Partitioning During Tank Processing**

**Principal Investigator:** Dr. Andrew R. Felmy

**Problem Area:** High-Level Waste

This proposal is to extend the work of an FY96 EMSP grant for examining the effects of organic chelate complexation of the speciation and solubility of Sr and trivalent actinides under strongly basic, high carbonate conditions, similar to those present in high-level waste tanks at U.S. Department of Energy storage sites. In the first three years of this research program a comprehensive experimental and modeling approach was implemented which focused on the displacement of Sr from organic chelators and the formation of important metal-chelate-hydroxide complexes for the trivalent actinides. This comprehensive approach involved coupled experimental solubility studies, spectroscopic measurements of solution speciation, molecular modeling studies which yielded information on species structure and energetics, and thermodynamic modeling efforts using the Pitzer thermodynamic model which is valid to high ionic strengths. Using this approach, research studies were completed on Sr and the trivalent actinide analog Eu(III) on four of the most important chelates in tank waste: EDTA, HEDTA, NTA, and IDA as well as on the important inorganic ligands, hydroxide and carbonate. All of these research results were published in the open literature. Although these studies have already proven useful in several waste tank applications, the complexity of many of the wastes, specifically with respect to ligand concentration and complexity of many of the wastes, specifically with respect to ligand concentration and competing metal content, shows that continued research is required in order to apply these results to a wide range of tank compositions.

Based upon our results, we proposed: 1) extension to important chelates not previously studied, 2) studies of competing metal ions, and 3) specific studies using Am(III)/Cm(III). The chelate complex studies will directly extend our previous research on EDTA, HEDTA, NTA, and IDA to citrate and oxalate. In addition, we propose to address the possible formation of mixed ligand-ligand complexes for Eu(III) in EDTA-HEDTA, EDTA-NTA, HEDTA-NTA, and chelate-carbonate solutions. The competing metal studies will address Ni, Al, Mn, and Fe. These studies will extend our previous work on the competing metal Ca. These fundamental data on chemical speciation and solubility will then be used to develop highly accurate thermodynamic models, which are valid to high ionic strength. Such thermodynamic models are widely used by scientists and engineers at Hanford and other DOE sites to help develop improved waste disposal technologies.

## **Annual Progress Report**

**2001 Progress Report**

**2002 Progress Report**

# **Environmental Management Science Program Research in Washington**

## **Pacific Northwest National Laboratory**

### **73750 – Radiation Effects in Nuclear Waste Materials**

**Principal Investigator:** Dr. William J. Weber

**Problem Area:** High-Level Waste

The objective of this project is to develop a fundamental understanding of radiation effects in glasses and ceramics, as well as the influence of solid-state radiation effects on aqueous dissolution kinetics. This study will provide the underpinning science to develop improved glass and ceramic waste forms for the immobilization and disposition of high-level tank waste, excess plutonium, plutonium residues and scrap, other actinides, and other nuclear waste streams. Furthermore, this study will develop predictive models for the performance of nuclear waste forms and stabilized nuclear materials. The research focuses on the effects of alpha and beta decay on defect production defect interactions, diffusion, solid-state phase transformations, gas accumulation, and dissolution kinetics. Plutonium incorporation, gamma irradiation, ion-beam irradiation and electron-beam irradiation are used to simulate the effects of alpha decay and beta decay on relevant glasses and ceramics in experimental studies. Computer simulation methods are used to provide an atomic-level interpretation of experimental data, calculate important fundamental parameters, and provide multiscale computational capabilities over different length (atomic to macroscopic) and time (picoseconds to millennia) scales.

## **Annual Progress Report**

### **2001 Progress Report**

### **2002 Progress Report**

# **Environmental Management Science Program Research in Washington**

## **Pacific Northwest National Laboratory**

### **73759 – Computational Design of Metal Ion Sequestering Agents**

**Principal Investigator:** Dr. Benjamin P. Hay

**Problem Area:** High-Level Waste

Metal ion recognition is critical in the development of sensors (detection of species in groundwater and chemical process streams), separating agents (removal of radionuclides and other ionic metals from nuclear waste, contaminated soils, and groundwater), and improved analytical techniques (separation and concentration of dilute analytes). We propose to continue our development of a computational approach toward the discovery of new ligand architectures for the selective complexation of radioactive metal ions of concern to the U.S. Department of Energy (DOE). To achieve this objective, we propose to 1) mine the Cambridge Structural Database and use electronic structure calculations to investigate the structure and energetics of metal ion-donor group interactions, 2) incorporate this information within the framework of a molecular mechanics model, and 3) apply the model to correlate ligand structure with reactivity toward metal ions. This research will provide the capability to screen sets of proposed ligand architectures, that is, select the best members from a set of possible candidates, before synthesis and testing. In addition, we propose to 4) use molecular structure building software to generate large numbers of candidate ligand architectures for given sets of donor groups, 5) couple the molecular structure builder with the screening capability, and 6) apply this tool to identify ligand architectures that will exhibit enhanced metal ion recognition.

These new capabilities will be applied to ligand systems identified under other DOE- sponsored projects where studies suggest that modifying existing architectures will lead to dramatic enhancements in metal ion binding affinity and selectivity. With this in mind, we will collaborate with Professors R. T. Paine (University of New Mexico) and K. N. Raymond (University of California, Berkeley) and Drs. B. A. Moyer and G. M. Brown (Oak Ridge National Laboratory) to obtain experimental validation of the predicted new ligand structures.

#### **Goals:**

Organic ligands with a high degree of metal ion recognition are essential precursors for developing separation processes and sensors for metal ions. Since the beginning of the nuclear era, much research has focused on discovering ligands that target specific radionuclides. Members of the Group IA and 2A cations (Cs, Sr, Ra) and the f-block metals (actinides and lanthanides) are of primary concern to DOE. Although there has been some success in identifying ligand architectures that exhibit a degree of metal ion recognition, the ability to control binding affinity and selectivity remains a significant challenge. The traditional approach for discovering such ligands involves lengthy programs of organic synthesis and testing that, in the absence of reliable methods for screening compounds before synthesis, have resulted in much wasted research effort.

We propose to strengthen the traditional approach with the computer-aided design of new and improved host molecules. Accurate electronic structure calculations can be coupled with experimental data to provide fundamental knowledge about ligand structure and the nature of metal-donor group interactions (design criteria). This information can be incorporated within a molecular mechanics model to provide a tool for screening proposed ligand architectures, that is, for selecting the best members from a set of potential candidates. Using combinatorial methods, molecule building software can generate large numbers of candidate architectures for a given set of donor groups. This proposal seeks to develop and apply these techniques for discovering novel ligand architectures that provide the maximum complementarity and preorganization for targeted metal ions. The specific goals of this project are as follows:

- to further understand the structural and energetic aspects of individual donor group—metal ion interactions —and incorporate this information within the framework of a widely used and available molecular mechanics model, MM3.
- to further develop and evaluate approaches for correlating ligand structure with reactivity toward metal ions, i.e., screening capability.
- to use molecule structure building software to generate large numbers of candidate ligand architectures for given sets of donor groups.
- to screen candidates and identify ligand architectures that will exhibit enhanced metal ion recognition.

Successful completion of this study will yield molecular-level insight into the role that ligand architecture plays in controlling metal ion complexation and provide a computational approach to ligand design. Technological development from this science is readily envisioned. Metal ion recognition is critical in the development of sensors (detection of species in groundwater and chemical process streams), separating agents (removal of radionuclides and other ionic metals from nuclear waste,-contaminated soils, and groundwater), improved analytical techniques (separation and concentration of dilute analytes), medicine (encapsulation of radionuclides used in cancer treatments, therapeutic agents for metal intoxication, models to study enzyme function), and homogenous catalysts (control of selectivity and activity).

## **Annual Progress Reports**

### **2002 Progress Report**

# Environmental Management Science Program Research in Michigan

## The University of Michigan

### 73762 – Radiation Effects on Sorption and Mobilization of Radionuclides during Transport through the Geosphere

**Principal Investigator:** Dr. Lu-Min Wang

**Problem Area:** High-Level Waste

Site restoration activities at DOE facilities and the permanent disposal of nuclear waste inevitably involve understanding the behavior of materials in a radiation field. Radionuclide decay and associated radiation effects lead to physical and chemical changes in important properties (e.g., sorption and cation exchange capacity). During waste processing and site restoration, materials can be exposed to radiation fields that exceed  $10^4$  rad/hr. The radiation exposure is due to the incorporation or sorption of long-lived actinides (e.g.,  $^{237}\text{Np}$ ) and fission products (e.g.,  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$ ). Thus, the effect of radioactive decay processes on waste processing materials (e.g., zeolites and silicotitanates) and geologic materials (e.g., colloidal clays and zeolites during transport through the vadose zone) are an important aspect of understanding the long-term fate and mobility of radionuclides in the geosphere.

During the past three years, we have evaluated radiation effects in selected near-field materials in accelerated laboratory experimental utilizing energetic electrons and ions and *in situ* transmission electron microscopy (TEM). Zeolites and layered silicates were irradiated. These materials were found to be highly susceptible to irradiation-induced solid-state amorphization. The critical doses for complete amorphization of these phases are as low as  $<0.1$  displacement per atom (dpa) or  $10^8$  GY in ionization energy deposition (i.e., the dose for a zeolite with 10 wt.% loading of  $^{137}\text{Cs}$  in 400 years). Even partial amorphization will cause a dramatic reduction (up to 95%) in ion-exchange and sorption/desorption capacities for radionuclides, such as Cs and Sr. Because the near-field or chemical processing materials, e.g., zeolites or crystalline silicotitanate (CST), will receive a substantial radiation dose after they have incorporated radionuclides, our results suggest that radiation may, in some cases, retard the release of sorbed or ion-exchanged radionuclides. These results have a direct bearing on repository performance assessments (e.g., the extent to which zeolites can retard the release of radionuclides) and on the technologies used to process high-level liquid waste (e.g., separation of  $^{137}\text{Cs}$  from HLW using CST at the Savannah River Site).

We propose to expand our study of radiation effects on the sorption and ion-exchange capacities of clays and zeolites by applying newly designed experimental methods. The radionuclides to be studied include Cs, Sr, U, and Se. These nuclides are important because: 1) they represent a range of sorptive behavior that should bracket the behavior of most other radionuclides (except  $^{99}\text{Tc}$ ) and 2) they are considered to make important contributions to total radiation exposures, as illustrated in the recent Total Systems Performance Assessment-Viability Assessment of the proposed repository at Yucca Mountain.

Selected clay and zeolite samples will be irradiated with high energy electrons, high energy ions and neutrons to simulate the radiation effects from a variety radioactive decay processes at a much accelerated rate using a unique combination of irradiation facilities available at the University of Michigan (the Ford Nuclear Reactor and the Michigan Ion Beam Laboratory). Ion exchange/sorption experiments will be conducted on samples irradiated to various doses to determine the impact of the radiation effects on the sorption capacity and retention of radionuclides. We also propose the use of novel ion implantation and surface analysis techniques, e.g., atomic force microscopy and Z-contrast high resolution scanning transmission electron microscopy (STEM), in order to identify atomic-scale effects of radiation damage associated with single or small clusters of radionuclides sorbed onto mineral surfaces.

Clay and zeolite colloids have recently been reported to be responsible for the migration of Pu for distances greater than one kilometer at the Nevada Test Site. We plan to use high resolution and analytical electron microscopy to characterize the different types of colloids present at the Nevada Test Site and at Hanford



(with samples provided by collaborators at Sandia National Laboratories and Lawrence Livermore National Laboratory).

The results of this research will provide a fundamental understanding of retention or release of radionuclides from geologic materials (clays, zeolites and colloids) in radiation-fields.

## **Annual Progress Reports**

### **2001 Progress Report**

# Environmental Management Science Program Research in California

## Lawrence Berkeley National Laboratory

### 73778 – Research Program to Investigate the Fundamental Chemistry of Technetium

**Principal Investigator:** Dr. David K. Shuh

**Problem Area:** High-Level Waste

Technetium presents a number of impediments to the disposition of the legacy nuclear waste found in tank farms at the Hanford and Savannah River sites. Reduced technetium complexes have been found in some waste tanks at Hanford, which greatly complicates the removal of technetium from these wastes. Our research has solidly demonstrated that pertechnetate,  $\text{TcO}_4^-$ , is reduced by radiolysis. This work provides evidence that the Tc(IV) complexes are  $(\text{diol})_4\text{Tc}_2(\text{i-O})_2$ , where diol is a diolate ligand such as ethylene glycol. Based on these results, new research will investigate the chemistry of these Tc(IV) complexes with an emphasis on oxidation and ligand exchange reactions. Knowledge gained from these investigations will provide a basis for removing these Tc(IV) complexes from waste streams.

Our research has shown that in cement waste forms,  $\text{TcO}_4^-$  is reduced to Tc(IV) by the blast furnace slag additive. Over a period of years, the resulting Tc(IV) species oxidizes back to  $\text{TcO}_4^-$ . These results highlight the fact that the stability of Tc(IV) in other waste forms is unknown. Using the experience and techniques developed for the cement studies, the stability and speciation of technetium in glass and ceramic waste forms will be examined to determine if technetium is similarly sensitive to oxidation. Low-temperature, sol-gel routes for the incorporation of technetium into ceramics, starting from  $\text{TcO}_4^-$  will be investigated. This fundamental information on the stability of technetium in several waste forms will provide an improved basis to evaluate different immobilization schemes for technetium.

## Annual Progress Report

[2001 Progress Report](#)

[2002 Progress Report](#)

# **Environmental Management Science Program Research in Tennessee**

## **Oak Ridge National Laboratory**

### **73803 – Next Generation Extractants for Cesium Separation from High-Level Waste: From Fundamental Concepts to Site Implementation**

**Principal Investigator:** Dr. Bruce A. Moyer

**Problem Area:** High-Level Waste

This renewal proposal unites expertise at Oak Ridge National Laboratory (ORNL), Pacific Northwest National Laboratory (PNNL), Virginia Polytechnic Institute & State University, and IBC Advanced Technologies, Inc. to answer fundamental questions addressing the problem of cesium removal from high-level tank waste. As such, this proposal seeks to pursue that part of the first performance period that attracted the greatest interest on the part of a potential user, namely the High-Level Waste Salt Disposition Team at the Savannah River Site. Efforts will focus on novel solvent-extraction systems containing designed calixcrown extractants, alcohol synergists, and alkylamines for optimized cesium binding and release. Synthesis of the new solvent components will be performed at ORNL, Virginia Tech, and IBC based on principles drawn from the prior EMSP research period (Project NO. 55087) and ligand design described under a separate proposal to the EMSP by Benjamin Hay at PNNL. Extraction behavior will be surveyed to assess the effectiveness of candidate solvent systems. Systematic distribution measurements will be modeled toward a thermodynamic understanding of controlling equilibria, especially ion partitioning and complexation. Structure-function relationships will be deduced with the aid of the PNNL molecular modeling and structural results from X-ray crystallography. The overall objective is a significant advance in the predictability and efficiency of cesium extraction from high-level waste in support of potential implementation at USDOE sites.

## **Annual Progress Report**

### **2001 Progress Report**

### **2002 Progress Report**

# **Environmental Management Science Program Research in New York**

## **Brookhaven National Laboratory**

### **73824 — Reactivity of Peroxynitrite: Implications for Hanford Waste Management and Remediation**

**Principal Investigator:** Dr. Sergie Lymar

**Problem Area:** High-Level Waste

The objective of the proposed research is to provide quantitative mechanistic information relevant to: (i) the extent of radiation-induced accumulation of peroxynitrite in the Hanford waste and its roles in waste degradation and (ii) the potential applications of peroxynitrite in remediation technologies.

Hanford radioactive waste contains large amounts of solid nitrate salts and their saturated solutions. Our studies within the previous EMSP funded period suggest that radiation-induced isomerization of nitrate into peroxynitrite, particularly in solid waste, could result in considerable accumulation of chemical energy in the form of this powerful oxidizing agent, which may present a reactive hazard upon dissolution of the waste for removal. Equally important, peroxynitrite produced by radiation in the liquid waste can contribute to oxidative modification of organic compounds in the waste storage tanks. At the same time, our data point to the potential for incorporating this very strong and inexpensive oxidant into the waste remediation technologies. These applications include mineralization of the organic waste components and removal of chromium from the waste using controlled catalytic oxidation by peroxynitrite; the steps that would greatly increase waste compatibility with vitrification-based disposal technologies and may result in considerable cost savings.

The proposed studies include: (1) Determinations of the peroxynitrite yields under different types of radiation in chemical mixtures simulating the various phases of Hanford waste. (2) Time-resolved mechanistic studies of the direct radiation effects in solid nitrates and their concentrated solutions. (3) Determination of the optimal conditions for carbon dioxide- and proton-catalyzed oxidation of organic complexants by peroxynitrite. (4) Evaluation of the feasibility of using peroxynitrite for oxidative dissolution of chromium hydroxide.

This research will utilize a wide range of specialized experimental facilities available within the Brookhaven National Laboratory including our state-of-the-art picosecond electron pulse radiolysis facility (with time-correlated laser detection capability), a Van de Graff accelerator, gamma and neutron radiation sources. Kinetic measurements will be supported by chemical product analyses and structural characterizations; the latter will use the x-ray diffraction and x-ray spectroscopic facilities at BNL National Synchrotron Light Source.

Collectively, these studies will analyze the reactivity of peroxynitrite in relation to Hanford problems and thereby contribute to more informed decisions concerning disposal options.

## **Annual Progress Report**

### **2001 Progress Report**

### **2002 Progress Report**

# Environmental Management Science Program Research in California

## The University of California - Davis

### 73827 - Non-Invasive Diagnostics for Measuring Physical Properties and Processes in High Level Wastes

**Principal Investigator:** Dr. Robert L. Powell

**Problem Area:** High-Level Waste

The target of the ultrasonic measurements is the local shear rate as determined from the measured local velocity in the pipe. This may be achieved by using an ultrasonic reflection-mode (pulse-echo) Doppler velocity mapping system. The principle of operation of the system is as follows: Ultrasonic transmission time – of- flight measurements can be used to determine the integrated line of sight acoustic velocity in the fluid. If the fluid contains scattering particles, then a coherent reflection system can be used to measure the Doppler frequency shift caused by the fluid flow. The magnitude of the Doppler shift can be used to determine the fluid velocity. Applying a sequence of range gates to the Doppler measurements allows determination of the fluid velocity profile along the line of sight of the ultrasonic transducer. If the acoustic velocity is uniform across the cross section of the pipe, and is axisymmetric then this range-gated ultrasonic Doppler data can provide accurate measurement of the fluid velocity profile.

However, in pipes involving flow of complex fluids of unknown or varying properties, both the fluid velocity profile and the acoustic velocity are expected to be non-uniform across the cross-section of the pipe. The time-of-flight acoustic transmission measurement will be in error if the fluid velocity is not taken into account, and the reflection Doppler measurement will be in error if the acoustic velocity profile is not known. This will cause a distortion of the fluid velocity profile measured by the ultrasonic Doppler system, since the Doppler shift is proportional to the acoustic velocity.

A single line measurement cannot accurately solve the complex pipe flow velocity program. The transmission measurement can only solve for the average acoustic velocity, not the acoustic velocity profile. The reflection Doppler measurement requires the acoustic velocity profile in order to determine the desired fluid velocity profile. A single line-of-sight measurement system does not provide enough information to simultaneously solve for both the acoustic and the fluid velocities.

To circumvent this difficulty, we propose a real-time tomographic ultrasonic Doppler velocimeter system. This system will utilize a number of ultrasonic transmission and reflection measurements along two orthogonal sets of parallel acoustic lines of sight as depicted in Figure 1. The fluid velocity profile and the acoustic profile can be determined by iterative application of the following two steps.

- (1) Reflection Doppler measurement can be used to determine the approximate fluid velocity profile along each line-of-sight assuming that the acoustic velocity is known (initially constant).
- (2) Transmission measurements of time-of-flight between opposing transducers will allow measurement of the integrated line-of-sight acoustic velocity at a number of positions across the pipe cross-section. Utilizing tomographic inversion, the acoustic velocity at each intersection point can be determined assuming that the fluid velocity is known (initially assumed known).

Once the shear rate distribution,  $\gamma(r)$ , in the pipe is measured, then the rheology of the mixture may be determined using the measurement of pressure drop,  $\Delta p$  in the pipe over a pipe length,  $L$ . Then the shear stress distribution  $\sigma(r)$ , may be found from the following relation.

$$\sigma(r) = (\Delta p / L)(r/2)$$

The plot of shear rate,  $\dot{\gamma}(r)$ , versus the shear stress,  $\sigma(r)$ , is the flow curve or the rheology of the fluid within the desired range.

### **Purpose**

The objectives of this project are:

- 1) to extend the range and applicability of ultrasonic Doppler velocity and measurement and rheometry to representative waste slurry pipeline.
- 2) To measure the speed of sound distribution within a slurry flowing in the pipe and correlate this with solids concentration and mass flow rate
- 3) To demonstrate particle sedimentation rate and interface measurement in using ultrasonic techniques.

### **Annual Progress Report**

#### **2001 Progress Report**

#### **2002 Progress Report**

# Environmental Management Science Program Research in Indiana

## University of Notre Dame

### 73832 – The NO<sub>x</sub> System in Homogeneous and Heterogeneous Nuclear Waste

**Principal Investigator:** Dr. Dan Meisel

**Problem Area:** High-Level Waste

The objective of this research is to develop quantitative understanding and predictive computer modeling capabilities of the chemistry in highly-concentrated homogeneous and heterogeneous simulants of high level waste.

The extension request focuses on two directions:

1. The effects of radiolytically initiated oxidation reactions of organic chelators by reactive radicals, primarily of the NO<sub>x</sub> family at realistic salt concentrations, and
2. The effect of solid/liquid particle interfaces on these reactions and on gas generation rates.

The former will focus on the development of theoretical, computational, and experimental descriptions of the chemistry of high level waste (HLW) in highly concentrated solutions. The latter will experimentally determine the yields of gases generated radiolytically at the surfaces of wet powders. The former will allow the prediction of the consequences of various scenarios that occur on handling liquid HLW (e.g. dilution, stirring, transporting of the convective layer among waste tanks). The latter simulates the sludge that remains in the tanks after volume reduction and removal of the liquid waste to a "Defense Waste Vitrification" facility.

We propose to:

- a. Develop a model and corresponding computer code to describe the effects of the high salt concentrations on solvation of the radical and radical ions of interest in this proposal.
- b. Calculate the electronic structure and properties of these radicals and radical ions including microsolvation, dielectric, and ionic strength effects. Determine the mechanisms of their interaction with complexants and radicals derived from them. Predict product distributions and rates of formation.
- c. Measure rate constants for the key reactions between NO<sub>x</sub> radicals and complexants and between organic radicals and NO<sub>x</sub><sup>-</sup> anions. Use these rate constants to check and augment the computed parameters of the model being developed to predict the behavior in the tanks.
- d. Synthesize powders of small particles of solids of the relevant materials; modify their surfaces to include various adsorbates of interest. Measure the yield of gases generated from these sludge simulants upon irradiation at various levels of wetting.
- e. The end product for the homogeneous tasks will be a computer model that will allow calculations of the pathways for oxidation of organics, their rate constants under various conditions and the radiolysis products. The heterogeneous task will provide experimental data to determine whether water at the particulate surface behaves as bulk water, at what levels of wetting does it deviate, and what are the new yields. Together, combined with our earlier studies and the ongoing related project at PNNL, we will provide a comprehensive, quantitative description having predictive capabilities for the waste chemistry.

## **Annual Progress Report**

**2001 Progress Report**

**2002 Progress Report**



# Environmental Management Science Program Research in Georgia

## School of Earth and Atmospheric Sciences

### 73859 – Quantify Silica Reactivity in Subsurface Environments: An Integrated Experimental Study of Quartz and Amorphous Silica to Establish a Baseline for Glass Durability

**Principal Investigator:** Dr. Patricia M. Dove

**Problem Area:** High-Level Waste

An immediate EM science need is a reliable kinetic model that predicts long-term waste glass performance. A framework for which the kinetics of mineral-solution reactions can be used to interpret complex silicate glass properties is required to accurately describe the current and future behavior of glasses as synthetic monoliths or natural analogs. Reaction rates and mechanisms are essential elements in deciphering mineral/material reactivity trends within a compositional series or across a matrix of complex solution compositions. An essential place to start, and the goal of the proposed research, is to quantify the reactivity of crystalline and amorphous  $\text{SiO}_2$  phases in the complex fluids of natural systems.

There are important motivations for quantifying  $\text{SiO}_2$  reactivity in the fluids of subsurface environments. First, quartz and  $\text{SiO}_2$  glass are the compositional end-member crystalline and amorphous oxides to large classes of silicate minerals and glasses. Second, an understanding of fundamental controls on the reactivity of simple Si-O bonded phases establishes baseline behavior for silica phases widely found in waste storage environments. Host rock silicate minerals compromise >90% of the earth's crust and dominate virtually every repository rock-water system. Finally, complex silicate glasses will be the front line of defense in containing radioactive wastes in both interim and long-term storage strategies. However, we have little quantitative understanding of pure  $\text{SiO}_2$  reactivity in the solutes of natural and perturbed groundwaters even though current EM strategy calls for dispersal of waste into silica-based glass materials.

The EM investment in our current study to understand silica reactivity has yielded significant returns in new scientific knowledge while also producing new talent for the waste immobilization effort. We have shown that all major solutes found in natural subsurface waters enhance the reactivity of both crystalline and glassy forms of  $\text{SiO}_2$  (up to 114X!). Yet, reactivity trends in simple solute mixtures have a complex, non-linear responses. This is important to unravel because we have virtually no quantitative and mechanistic understanding of how (whether?) other solutes frequently found in the groundwater and soil solutions of pristine or contaminated areas interact with mineral surfaces to affect long-term reactivity. Further, there is little quantitative understanding of reaction rates in near-equilibrium solutions that typify natural fluid chemistries. Both of these issues are important because the available data suggest that solutes and reaction affinity controls on reactivity exert complex rate-enhancing as well as rate-inhibiting effects.

Our findings in EM 96-10 suggest that a fundamental and reliable predictive principle exists and this new knowledge has shown us how to establish this principle. Using new experimental and theoretical analyses, this renewal proposal seeks to determine baseline relations and use this knowledge to address the problem of how complex solute mixtures found in *real* solutions control long-term stability in corrosion. A general model for solute effects on reactivity will also quantify whether contaminant cations, Tc, Cs and Sr affect reactivity. The proposed research is an important opportunity to continue focusing our expertise in mineral-water interactions on this important problem. Given the experience of the P.I. and her publication record, the proposed research is a cost-effective approach to advancing basic and applied scientific knowledge of solute controls on silica reactivity in natural and engineered Earth Systems.

The research plan uses an integrated experimental approach to construct a quantitative model of solute controls on the reactivity of crystalline and glassy  $\text{SiO}_2$ . We will measure the dissolution rate of quartz and silica glass in a series of carefully selected mixed solute solutions over a range of pH and temperature. We will also determine the effect of reaction affinity on rate in DIW (control) and solute-bearing solutions by adjusting steady state silica concentrations produced during the dissolution reactions. The kinetic portion of

the study will be conducted in parallel with surface investigations of selected samples/conditions to resolve the controversy of reaction mechanism by conducting high-quality potentiometric surface titrations in the relevant solute-bearing solutions. This will settle long-standing questions of whether (how) solutes control mineral surface charge and reactivity. The quantitative information will be complemented by findings from *in situ* Atomic Force Microscopy (AFM) and *ex situ* analyses by XPS and Auger. Findings will establish quantitative relationships between silica reactivity and complex solution chemistries never investigated and are presently speculative at-best. Further, we will be able to uncover an underlying principle that governs how solutes affect silica reactivity in a systematic and predictable way. The scientific problems addressed in this proposal are ripe for advancement through a well- defined investigation that is certain to produce new and valuable kinetic data while developing a comprehensive model for complex solute controls on silica reactivity and durability.

## **Annual Progress Report**

### **2001 Progress Report**

# **Environmental Management Science Program Research in New York**

## **Syracuse University**

### **73896 – Acoustic Monitor for Liquid-Solid Slurries Measurements at Low Weight Fractions**

**Principal Investigator:** Dr. Lawrence L. Tavlarides

**Problem Area:** High-Level Waste

Treatment of radioactive wastes stored in tanks across the DOE complex will require real-time characterization and monitoring of the size and weight fractions of solids in slurries during retrieval and transport of material between tanks. In the privatization contract Hanford this need is of particular significance to meet the minimum physical property requirements for which a monitor to measure one to five weight percent solids within acceptable uncertainty levels is required. The proposed research will fabricate, commission and test an acoustic probe with appropriate instrumentation to demonstrate the capability to accurately measure weight percent solids in slurries at these low levels. The probe will be tested in the flow loop at Oak Ridge National Laboratories for well-defined surrogate slurries for Hanford. The theory for acoustic wave propagation in solid-gas-liquid systems developed and confirmed in the first funding period will be the basis for analysis and interpretation of the acoustic signals.

## **Annual Progress Report**

**2001 Progress Report**

**2002 Progress Report**

# **Environmental Management Science Program Research in Missouri**

## **University of Missouri-Rolla**

### **73976 – Iron Phosphate Glasses: An Alternative for Vitrifying Certain Nuclear Wastes**

**Principal Investigator:** Dr. Delbert E. Day

**Problem Area:** High-Level Waste

Borosilicate glass is the only material currently approved and being used to vitrify high level nuclear waste. However, some waste feeds in the U.S. contain components which are poorly soluble or chemically incompatible in borosilicate glasses [1-5]. Current plans call for vitrifying even these problematic waste feeds in borosilicate glasses after the original waste feed has been pre-processed and/or diluted to compensate for the incompatibility. However, these pre-treatment processes, as well as the larger waste volumes resulting from dilution, will greatly increase the DOE's cost of cleaning up the former nuclear weapons production facilities. At least some, if not all of this additional cost can be avoided if a number of alternative waste glasses were available and used to vitrify those specific waste feeds that are poorly suited for borosilicate glasses.

With funds [6] from the Environmental Management Science Program (EMSP), U.S. Department of Energy, we have developed [7-24] an alternative waste form based on a new family of iron phosphate glasses. These iron phosphate glasses appear to be an excellent candidate for vitrifying many waste feeds, including those poorly suited for borosilicate glasses. Our work, done in collaboration with scientists from *Pacific Northwest*, *Lawrence Berkeley*, *Lawrence Livermore*, and *Argonne* national laboratories and the *Westinghouse Savannah River* and *Naval Research* laboratories, strongly suggests that the iron phosphate glasses are a low cost and technically effective alternative to borosilicate glasses for vitrifying selected nuclear wastes.

The scientific and technical knowledge base that is needed to vitrify nuclear waste in iron phosphate glasses on a production scale is currently lacking. In addition, the high priority waste that are likely to cause problems in borosilicate melts need to be identified and property data needs to be acquired for iron phosphate waste forms made from these wastes. The research described herein is designed to provide the important information that is still needed before iron phosphate glasses can be used to vitrify those nuclear wastes which are poorly suited for borosilicate glasses.

## **Annual Progress Report**

**2001 Progress Report**

**2002 Progress Report**

# Environmental Management Science Program Research in Kansas

## University of Kansas

### 74019 – The Supramolecular Chemistry of Anion Recognition for Anions of Environmental Relevance

**Principal Investigator:** Dr. Kristen Bowman-James

**Problem Area:** High-Level Waste

In the High-Level Waste (HLW) area a key science need has been identified in the phase separation and crystallization area as obtaining a clearer understanding of components of waste that have low solubility's on glass. Sulfate has been identified as a particularly difficult problem in vitrification of tank wastes at Hanford because of its low solubility (typically <1%) in borosilicate glass. Sulfate management in low activity waste via pretreatment, vitrification, and off gas approaches is recognized as having substantial benefit. A major thrust of this project is entails the exploration of principles of recognition and separation of sulfate. Nitrate is also present in large quantities in tank wastes and removal of sodium nitrate could greatly reduce the volumes of these wastes. Hence, separation of the two salts has been the object of major investigations aimed at ultimately reducing the number of expensive HLW glass canisters that must be produced and stored. Additionally,  $^{137}\text{Cs}^+$  is a major contaminant of nuclear wastes at several sites in the United States. The goal is to identify selective extraction reagents for these contaminants, and thus to greatly reduce the costs of remediation, especially that of the vitrification and final disposal.

This effort integrates the design of selective receptors for anions of critical importance to the DOE with corollary receptors for associated cations. Sulfate and Nitrate anions have been selected as key contaminants with  $^{137}\text{Cs}$  the targeted cation. A key goal of this research is to apply the basic foundations of knowledge obtained for selective anion binding on previous research to continued research using dual receptor systems. It is anticipated that the resulting systems will be capable of being employed directly in the remediation process. The focus will be on developing robust and versatile systems that are capable of functioning throughout a wide pH range that are also soluble in organic systems. The work will be conducted in three parts.

Part I. An in-depth study of the binding properties of the two ions with dual anion-cation receptor systems will be undertaken. Commercially available crown ethers will be used for cation binding, while primarily various polyamide receptors will be examined as anion binding agents. Anion and cation selectivities as a function of the co-ions and co-receptors will be established in order to design the optimum systems for applications in separations.

Part II. A relatively new method will be used to probe the chemistry of transport across liquid-liquid interfaces. The approach is different from conventional methods of selective electrode systems and is known as the Interface between Two Immiscible Electrolyte Solutions (ITIES). The selective transfer of ions across the aqueous/organic interface is important to the development of analytical techniques and is also key to understanding solvent extraction processes. By using this relatively new analytical methodology, the thermodynamics of the interfacial transfer can be used to probe the mechanisms of the transport at a molecular level. The dual receptor systems identified in part I as showing promise as selective binding agents will be examined in part II.

Part III. Of tantamount importance to this proposed project will be the liquid-liquid extraction studies using the concept of dual ion recognition and key receptor systems identified in part I and part II. The goal is to maximize the efficiency of the extraction process and to achieve highly selective sequestration of the targeted anions. Target salts will include  $\text{CsNO}_3$ ,  $\text{NaNO}_3$  and  $\text{Na}_2\text{SO}_4$ . Distribution studies will be performed using  $^{137}\text{Cs}$  and  $^{22}\text{Na}$  as tracers

## **Annual Progress Report**

**2001 Progress Report**

**2002 Progress Report**

# Environmental Management Science Program Research in Kansas

## The Pennsylvania State University

### 81866 – Development of Advanced Electrochemical Emission Spectroscopy for Monitoring Corrosion in Simulated DOE Liquid Waste

**Principal Investigator:** Dr. Digby MacDonald

**Problem Area:** High-Level Waste

The objectives of this program are to explore fundamental issues related to corrosion and stress corrosion cracking (SCC) of carbon and low alloy steels in simulated DOE liquid waste tanks and to use the data and information so obtained to develop corrosion and fracture mechanisms that are physically more accurate and of greater predictive power than those that currently exist. This need arises because, as outlined below, the currently employed slip/dissolution model for crack propagation is inconsistent with recently obtained experimental data and hence must be discarded or substantially modified. Furthermore, a great need exists for remote corrosion rate sensors that can be installed into the waste storage tanks to monitor the development of both general and localized corrosion damage. Once we have developed the advanced models they will be inserted into various codes for predicting the evolution of localized corrosion damage in DOE liquid waste storage tanks. The proposed work is a continuation of Project No. 60219 (Grant No. DE-FG07-97ER62515), "Development of Advanced Electrochemical Emission Spectroscopy for Monitoring Corrosion in Simulated DOE Waste," which is due for completion on September 30, 2001.

The project objectives will be accomplished by: 1) Continuing experimental and theoretical studies of passivity, including the development of the theory of the growth and breakdown of passive films on metal surfaces, to obtain better insight into the mechanisms of general corrosion and the initiation of localized corrosion; 2) Continuing our development of corrosion sensors that make use of electrochemical emission spectroscopy (EES) to obtain the "noise resistance" and hence the general corrosion rate of the steel in alkaline environments; 3) Experimentally measuring crack growth rate, acoustic emission signals, and coupling currents for fracture in carbon and low alloy steels as functions of mechanical (stress intensity), chemical (conductivity), electrochemical (corrosion potential, ECP), and microstructural (grain size, precipitate size and type, etc.) variables in a systematic manner, with particular attention being focused on the structure of the noise in the current and its correlation with the acoustic emissions; 4) Developing fracture mechanisms for carbon and low alloy steels that are consistent with the crack growth rate, coupling current data, and acoustic emissions; and 5) Inserting the advanced crack growth rate models for SCC into existing deterministic codes or predicting the evolution of corrosion damage in the DOE liquid waste storage tanks.

Recent experimental work on caustic cracking in tempered AISI 4340 steel (Project 60219) and on intergranular stress corrosion cracking (IGSCC) of sensitized Type 304 SS in high temperature dilute sulfate solution (at 250 °C) has shown that the crack internal and external environments are strongly coupled. This condition is required by the differential aeration hypothesis for localized corrosion and by the conservation of charge, which are embodied in the various "coupled environment" models that we have previously developed to deterministically predict crack growth. Coupling is manifest by current flow from the crack to the external surfaces, where the current is consumed by the reduction of a cathodic depolarizer (e.g., oxygen). The magnitude of the mean current appears to vary linearly with crack growth rate (CGR, as determined in the stainless steel work). If confirmed as a general relationship, coupling current versus CGR would provide a sensitive means of measuring the crack propagation rate, because of our ability to measure very small current accurately, and hence would give rise to entirely new, yet simple fracture monitors. More importantly from a fundamental mechanistic viewpoint, however, is the observation (in the case of the stainless steel) of structured noise in the coupling current that occurs as packages of 4 to 13 periodic oscillations separated by short periods of intense current activity. The individual periodic events are associated with a dimension of a few microns, whereas the packages are associated with features that are tens of microns in dimension (grains). The smaller dimension is far too large to be attributed to slip, which should have a dimension that is a small multiple of the Burger's vector, or a few nanometers. Instead, we

have tentatively attributed the periodic current oscillations to brittle micro fracture events occurring on an unfavorably oriented grain face (with respect to the stress) and the package with the number of events that is required to traverse the face. We have detected similar brittle micro fracture events during caustic cracking in AISI 4340 steel although in this case the data are consistent with many events occurring simultaneously across the crack front. It is evident from these initial studies that the coupling current provides an extraordinarily sensitive tool for relating crack tip processes to mechanical, chemical, electrochemical, and microstructural properties of the system and hence provides an unprecedented opportunity to define more accurately fracture mechanisms. We propose to do this by exploring the structure in the noise systematically as a function of various independent variables ( $K_I$ , conductivity, ECP, and grain size and other microstructural features), in order that the origins of the noise can be identified and understood. We will also measure acoustic emissions from the brittle fracture events and determine whether they correlate with the noise structure.

**This project began in 2001. The first progress report is expected in late 2003.**



## **Environmental Management Science Program Research in Illinois**

### **Illinois Institute of Technology**

#### **81867 – Foaming and Antifoaming in Radioactive Waste Pretreatment and Immobilization**

**Principal Investigator:** Dr. D. T. Wasan

**Problem Area:** High-Level Waste

The objectives of this proposed multidisciplinary, multi-organizational research effort are to develop a fundamental understanding of the physio-chemical mechanisms that produce foaming in the DOE High Level (HLW) and Low Activity (LAW) radioactive waste separation processes and to develop and test advanced antifoam/defoaming agents. The specific tasks to be undertaken are to 1) establish the effects of soluble and insoluble inorganic components and organic complexants on foam formation and stability in alkaline and acidic defense waste matrixes, 2) develop a fundamental understanding of the interaction of organic waste components with insoluble solid waste components, 3) develop and test advanced antifoam/defoamer agents on simulates of radioactive wastes, and 4) test and compare advanced antifoams with commercial antifoams using simulants and radioactive waste. Antifoams developed from this research will be tested using defense HLW radioactive wastes obtained from the Hanford and the Savannah River Site (SRS). Consequently, the work will be closely coupled to the needs of the DOE River Protection Project Waste and the SRS HLW, Alternative Salt Disposition Program and Defense Waste Processing Facility (DWPF). The results of this study will further enhance DOE and the commercial industry understanding of foam technology in alkaline and acidic three-phase (gas/liquid/solids) systems and thereby increase the throughput of planned and existing DOE radioactive waste pretreatment and immobilization processes. The proposed research will be a collaboration between the Illinois Institute of Technology (IIT) and Savannah River Technology Center (SRTC).

### **Annual Progress Reports**

#### **2002 Progress Report**

# Environmental Management Science Program Research in Washington

## Pacific Northwest National Laboratory

### 81883 – Mechanisms and Kinetics of Organic Aging and Characterization of Intermediates in High-Level Waste

**Principal Investigator:** Donald M. Camaioni

**Problem Area:** High-Level Waste

This is a renewal request for our 1998 EMSP project, “Mechanisms and Kinetics of Organic Aging in High Level Waste.” This project and a recently renewed EMSP project entitled “*The NO<sub>x</sub> System in Homogeneous and Heterogeneous Nuclear Waste*” (PI - D. Meisel of the Notre Dame Radiation Laboratory [NDRL]) have been and are planned to be closely coordinated as they have common objectives:

*To develop quantitative understanding and predictive computer modeling capabilities of the chemistry in high-level waste.*

This renewal proposal continues our focus on reactions of organic waste compounds with emphasis on

- Thermally-initiated organic reactions
- Theoretical characterization of intermediates
- Predictive model development

The primary focus of the NDRL project is on radiolytically-initiated oxidation reactions of organic chelators by reactive radicals, primarily the NO<sub>x</sub> family. The combined efforts of the two projects will provide comprehensive experimental, theoretical, and computational descriptions of HLW chemistry and contribute to the ability to predict the consequences of various scenarios that occur on handling HLW (e.g., dilution, stirring, transporting of the convective layer among waste tanks). The experimental effort will focus on the determination of the products, kinetics and mechanisms of organic reactions that occur in HLW. The theoretical characterization will complement the experimental effort providing information on intermediates and mechanisms that is not easily obtained by experiment.

Specifically, we propose to:

1. Measure rate constants for key reactions between nitrite ion and complexants and examine the role of Al. Use these rate constants to augment the radiolytic model being developed by the NDRL-led effort to predict behavior in the tanks.
2. Use a powerful computational protocol arrived at in our previous project to calculate accurately the electronic structure and properties of organic intermediates in aqueous medium, including thermochemical properties such as acidity ( $K_a$ ), redox potentials ( $E^0$ ), and reaction energies ( $H$  and  $G$ ).
3. Enhance and extend the methodology of part 2 to calculate solution properties of inorganic oxoanions, in particular those of Tc, and organic complexes of Tc.

In this proposal, we strive toward developing a computer model that will allow calculations of the pathways for redox reactions of organic compounds, their rate constants under various conditions and the products. Such a model will lead to predictive capabilities needed to make decisions as they arise relating to HLW. In our prior work, jointly with the NDRL researchers, we successfully modeled the radiolytic degradation of formate to carbonate in HLW simulants. The proposed research allows for continued development of this model. Mechanistic probe experiments have been designed to gain fundamental insight into mechanisms that operate during thermal degradations so that thermal and radiolytic processes may be integrated in the

model. Key kinetic data and thermodynamic properties relating to thermal reactivity will also be acquired so that rate-controlling and product-forming reactions can be predicted. Thermochemical properties of key intermediates will be determined to facilitate mechanism verification, structure/reactivity correlation, and prediction of reaction rates. We will use state-of-the-art computational methods to supplement the experimental effort. While current computational quantum chemical ‘black box’ models of solvation do not yet yield solvation data of sufficient accuracy for the organic radical ions of interest in HLW, our efforts, as part of the prior work, have led us to devise a unique and powerful ‘semi-empirical’ strategy that has the potential to circumvent the deficiencies of the models for these species. We will apply this protocol in support of the experimental investigations planned in this project. The same strategy should also prove successful for other important HLW species such as the oxoanions of Tc, Cr, and Se. In particular, organic complexants and radiation affect the speciation of Tc in HLW by redox reactions and the complexation of the Tc(IV) state that, as  $\text{TcO}_2$  is insoluble in alkaline solutions. The theoretical characterization of these species in their various oxidation states should provide valuable information regarding the chemistry and stability of these species in HLW.

## **Annual Progress Reports**

### **2002 Progress Report**

# **Environmental Management Science Program Research in Washington**

## **Pacific Northwest National Laboratory**

### **81887 – Precipitation and Deposition of Aluminum-Containing Phases on Tank Wastes**

**Principal Investigator:** Shas V. Mattigod

**Problem Area:** High-Level Waste

Aluminum-containing phases represent the most prevalent solids that can appear or disappear during the processing of radioactive tank wastes. Processes such as sludge washing and leaching are designed to dissolve Al-containing phases and, thereby, minimize the volume of high-level waste glass required to encapsulate radioactive sludges. Unfortunately, waste-processing steps that include evaporation can involve solutions that are supersaturated with respect to cementitious aluminosilicates that result in unwanted precipitation and scale formation. Of all the constituents of tank waste, limited solubility cementitious aluminosilicates have the greatest potential for clogging pipes and transfer lines, fouling highly radioactive components such as ion exchangers, and completely shutting down processing operations. Such a problem has already been encountered at the Savannah River Site, where the 3H evaporator has been shutdown since October 1999 due to the scaling and clogging caused by the precipitation of sodium aluminosilicate (zeolite) solids. Mineral precipitation has also caused plugging of highly radioactive components such as the cesium removal columns at the Savannah River Site. Such waste processing hiatus at SRS portends similar problems that could be encountered at other waste sites that would result in frequent interruption of the process and concomitant increases in time and cost of treating tank wastes. Unfortunately, there is limited information regarding the factors controlling the precipitation and redissolution of aluminosilicate (zeolitic) phases within the temperature regimes and the high alkaline and ionic strength environments of the waste tanks and the evaporators. Therefore, there is an urgent need for data to understand this phenomenon and develop means of avoiding problematic sludge processing steps.

Our research plan is designed to develop such data by studying the formation, solubilities, and transformations of cementitious aluminosilicates that may form under realistic waste processing conditions. These studies also include plans to evaluate the factors that promote heterogeneous nucleation and growth, identify the mechanisms of aluminosilicate scale formation, determine the role of selected organics to inhibit scale formation, and develop phase equilibrium diagrams as a tool to predict the solution conditions that will prevent precipitation of scale-forming aluminosilicates. We plan to use a combination of novel experimental methods such as nuclear magnetic resonance (NMR), small-angle x-ray scattering (SAXS), transmission electron microscopy (TEM), scanning electron microscopy (SEM), atomic force and scanning tunneling microscopy (AFM/STM) to investigate these processes. The data developed from this study will provide a reliable scientific basis for avoiding problematic sludge processing steps, and to identify and develop effective technologies to process retrieved sludges and supernatants before ultimate vitrification of wastes.

### **Annual Progress Reports**

#### **2002 Progress Report**

## **Environmental Management Science Program Research in Washington**

### **Pacific Northwest National Laboratory**

#### **81889 – Investigating Ultrasonic Diffraction Grating Spectroscopy and Reflection Techniques for Characterizing Slurry Properties**

**Principal Investigator:** Dr. Margaret S. Greenwood

**Problem Area:** High-Level Waste

The U.S. Department of Energy (DOE) has millions of gallons of radioactive liquid and sludge wastes that must be retrieved from underground storage tanks. This waste, in the form of slurries, must be transferred and processed to a final form, such as glass logs. On-line instrumentation to measure the properties of these slurries in real-time during transport is needed in order to prevent plugging and reduce excessive dilution. The research plan presented here, describes a collaborative effort between Pacific Northwest National Laboratory (PNNL) and the University of Washington to develop a *completely new method* for using ultrasonics to measure the particle size and viscosity of a slurry. The concepts are based on work in optics on grating-light-reflection spectroscopy (GLRS) at the University of Washington and some preliminary work on ultrasonic diffraction grating spectroscopy (UDGS) that has already been carried out at PNNL. The objective of the proposed research is to extend the GLRS theory for optics to ultrasonics, and to demonstrate its capabilities of UDGS. The viscosity of a slurry is measured by using the multiple reflections of a shear wave at the slurry-solid interface. The proposed ultrasonic method could result in an instrument that would be simple, rugged, and very *small*, allowing it to be implemented as part of a pipeline wall at facilities across the DOE complex.

### **Annual Progress Reports**

#### **2002 Progress Report**

# Environmental Management Science Program Research in Alabama

## University of Alabama

### 81891 – A New Class of Solvents for TRU Dissolution and Separation: Ionic Liquids

**Principal Investigator:** Robin D. Rogers

**Problem Area:** High-Level Waste

We propose to investigate Ionic Liquids (IL) as a new class of solvents for targeted dissolution and separation of transuranic elements (TRU). The proposed research will address three important areas; separation science, physical and chemical properties of IL, and metal ion speciation and coordination in IL. The separation science emphasis will investigate TRU element dissolution and partitioning behavior in liquid/liquid systems with a series of IL as the extracting phase. The development of new separations techniques will also be explored. Actinide speciation and coordination studies will probe the solution chemistry to aid in optimizing the separation schemes. IL thermal stability, radiolytic stability, and heat capacity measurements will be examined in relation to the use of IL as heat transfer media.

Ionic liquids represent a new type of solvent media which, as of yet, has not been developed and understood to maximize their impact. To better understand IL as solvents, several literature reports have related the properties of IL to those of known solvents, most resembling a short chain alcohol. However, IL can function in ways unlike molecular solvents. British Nuclear Fuels (BNFL) has a patent which describes a process where an IL,  $[C_4mim][NO_3]$ , can dissolve fuel cladding, but they then propose traditional PUREX processing to recover uranium and plutonium. It is our intention to investigate and develop IL as a new solvent system for use in processing and separations schemes, particularly targeted as alternative solvents for use in TRU recovery and processing where solvents such as kerosene, isopropyl benzene, and methyl ethyl ketone are necessary.

There are two colleagues that have agreed to advise us on the research and applications of the proposed project. Dr. Luis Nuñez (Chemical Technology Division at Argonne National Laboratory) has experience with separations and vitrification and has agreed to assist with experiments to investigate the radiolysis of IL. Dr. David Hobbs (Westinghouse Savannah River Company) will contribute to the proposal through technical assistance regarding waste form characterization.

The long range goals for this actinide research proposal include the development of liquid/liquid systems and other new methodologies for TRU separations based on a fundamental understanding of actinide speciation and coordination in IL. The goals will be pursued through a series of parallel objectives, which include:

- Examine Cs, Sr, Tc, and TRU partitioning in IL/aqueous systems
- Develop new IL for TRU separations
- Study the speciation and coordination of TRU elements in both hydrophilic and hydrophobic IL
- Investigate how aqueous phase composition affects the liquid/liquid partitioning behavior with particular emphasis on aqueous phases similar to those found in Department of Energy (DOE) related tank wastes

In addition, the long range goals for an in-depth study of IL include an analysis of heat transfer and radiolytic properties to examine the potential for IL applications in DOE related waste activities. Since the waste will innately generate intense fields from the radioactivity, radiolysis is common for both solvents and solutes in waste related processes. Thus, the stability of the separation process is jeopardized. However, if IL are stable in the presence of intense radioactivity or endure longer contact times without degradation, they may be more viable for incorporation into waste related separations. The following objectives will be pursued:

- Determine the stability of IL to thermolysis and radiolysis
- Investigate the unique heat transfer properties of IL for use in other processing steps

This proposal will advance the area of TRU chemistry and waste related activities in several aspects. In contrast to the molten fluoride salt and eutectic chloride salts previously used in reprocessing systems, IL have a unique solvent nature unlike high temperature melts. Depending on composition, they can offer a solvent environment with high ionic activity of  $\text{NO}_3^-$  or  $\text{Cl}^-$ . The study of TRU speciation and complexation behavior in IL will enhance the fundamental understanding of solutes in IL and, as a new solvent paradigm, extend the options available for waste processing issues. Metal ion complexation studies will aid in the design of new TRU extractants and to optimize liquid/liquid separation systems for radionuclide waste remediation. Separately, characterization of IL thermal and radiolytic stabilities may reveal the potential for IL as an example of completely new solvent media for a variety of high level radioactive waste applications.

## **Annual Progress Reports**

### **2002 Progress Report**

# **Environmental Management Science Program Research in Washington**

## **Pacific Northwest National Laboratory**

### **81893 – Physiochemical Processes Controlling the Source Term for Tank Residuals**

**Principal Investigator:** B. Peter McGrail

**Problem Area:** High-Level Waste

After remediation and closure of the high-level waste tanks at Hanford (and at other DOE sites), residual radionuclide bearing solids will remain in the form of sludge and hard heel adhering to the inner surfaces of the tanks. Radionuclide release from these residuals represents a potentially significant source of contaminants migrating in the sediments underlying the tanks. A recent composite analysis for the Hanford Site has shown the radionuclide source term from the residual solids to be one of the most significant long-term dose contributors on site, essentially equivalent in magnitude to a number of well-known discharges from leaking single-shell tanks. However, this assessment was based on a highly conservative release model for the tank residuals. The conservative model is being used in lieu of a true scientific understanding of the processes controlling the release rate from the sludge that is applicable to the Hanford vadose zone environment. Currently, the DOE is planning to spend hundreds of millions of dollars to remove 99% or more of the waste from Hanford high-level waste tanks that may have no real long-term environmental benefit. Through this project, we will significantly improve the fundamental scientific basis for estimating the release rate of <sup>99</sup>Tc, the principal long-term dose contributor from tank residual wastes.

We envision an improved conceptual model that considers diffusion of water and oxygen in the sludge under conditions of partial hydraulic saturation, but 100% relative humidity, consistent with the subsurface environment at Hanford. Key chemical processes are also considered, including the oxidation of reduced Tc compounds in the sludge, and the chemical changes in sludge phase assemblage that will occur over time. A combination of novel experimental methods is proposed to investigate these processes. This comprehensive study will provide a sound technical basis for the DOE and local stakeholders to make more informed cost/benefit/risk decisions regarding closure of Hanford high-level waste tanks.

### **Annual Progress Reports**

#### **2002 Progress Report**



## **Environmental Management Science Program Research in Idaho**

### **Idaho National Engineering and Environmental Laboratory**

#### **81895 – Fundamental Chemistry of the Universal Extractant (UNEX) for the Simultaneous Separation of Fission Products and Transuranics from High-Level Waste Streams.**

**Principal Investigator:** Dr. R. S. Herbst

**Problem Area:** High-Level Waste

Collaborative research by the Idaho National Engineering and Environmental Laboratory and the Khlopin Radium Institute (St. Petersburg, Russia) has already developed and validated the concept of a Universal Extraction (UNEX) solvent for simultaneously removing radioactive strontium, cesium, and transuranics from acidic aqueous waste streams in a single process. These development efforts can be best described as a “brute force” endeavor, where extractants were simply evaluated for extraction efficiency. No fundamental data exist on the chemistry of the UNEX solvent or its molecular interactions with extracted metal ions. We propose to conduct research that experimentally combines classical chemical techniques with advanced instrumental methods to elucidate the mechanisms of simultaneous metal extraction, along with subsequent deployment of Extended X-Ray Absorption Fine Structure (EXAFS) experiments to identify and explain the coordination geometries of extracted metal ions. This project will develop a fundamental understanding of the complicated extraction chemistry of the multi-component UNEX extractant. The results will facilitate enhancements to the process chemistry—increasing the efficiency of the UNEX process, minimizing primary and secondary waste streams, and enhancing compatibility of the product streams with the final waste forms—with the global objective of implementing the UNEX process at the industrial scale. This project specifically addresses the EMSP solicitation (LAB-01-16) call for research into “high-efficiency, high-throughput separation methods” that can “remove multiple radionuclides in a single step.” This project also directly addresses Tanks Focus Area FY01 Science Need S-WT-09-01 and INEEL site technology coordination group (STCG) needs ID-2.1.06 and ID-2.1.57.

### **Annual Progress Reports**

#### **2002 Progress Report**

# **Environmental Management Science Program Research in Washington**

## **Pacific Northwest National Laboratory**

### **81896 – Speciation, Dissolution, and Redox Reactions of Chromium Relevant to Pretreatment and Separation of High-Level Tank Wastes**

**Principal Investigator:** Dr. Dhanpat Rai

**Problem Area:** High-Level Waste

Chromium, one of the problematic elements in tank sludges, is considered the most important constituent in defining the total volume of high-level waste (HLW) glass. Current sludge washing processes are not effective in removing Cr, which results in production of an unacceptably large volume of HLW glass. Therefore, Cr chemistry studies relevant to tank conditions were initiated about two and a half years ago (EMSP project 65368) to obtain fundamental data necessary to develop pretreatment processes for removing Cr from sludges. A combination of techniques used to obtain structural information on the Cr(III) aqueous species has shown that a wide variety of Cr(III) species, from monomeric to highly polymeric, can be present in acidic to strongly alkaline solutions. This fundamental information has aided 1) the development of a thermodynamic model for predicting the solubility of  $\text{Cr}(\text{OH})_3(\text{am})$ , one of the important solid phases identified in tank sludges, in dilute to concentrated NaOH and  $\text{NaNO}_3$  solutions representing electrolytes present in tanks, and 2) the mechanistic understanding of the reactivity of  $\text{H}_2\text{O}_2$  and  $\text{K}_2\text{S}_2\text{O}_8$  in oxidation of Cr(III) species. The solubility model was tested with leaching results for sludges from 14 different Hanford tanks. Close agreement was observed between the predicted and observed Cr concentrations in the leachate that primarily contains NaOH. However, differences as large as three orders of magnitude between the predicted and the observed Cr concentrations were observed when the leachate contains a complex suite of electrolytes. These results are being incorporated into the Tanks Focus Area Environmental Simulation Program (ESP).

Extensive studies conducted under our current EMSP project 65368, which are summarized in this renewal application, clearly identify four areas in which additional research on fundamental aspects is needed to develop effective pretreatment processes and predictive models for removing Cr from sludges. These four areas are 1) the solubility of other important Cr solid phases, in addition to  $\text{Cr}(\text{OH})_3(\text{s})$ , that have been identified in tank sludges, 2) the effect of multiple electrolytes, in addition to NaOH and  $\text{NaNO}_3$  studied previously, on the solubility of important Cr solids, 3) the effect of the nature of Cr solids and corresponding aqueous species on their redox reactivity with additional oxidants that are proposed for use in oxidative sludge washing, and 4) validation of the data and models with more results from actual sludge washing and incorporation of the thermodynamic data into the ESP model that is extensively used at Hanford, Savannah River, and other Department of Energy (DOE) sites. The experience accumulated in previous studies and the methodologies developed under the current EMSP will help considerably in the success of this proposed EMSP project.

## **Annual Progress Reports**

### **2002 Progress Report**

# **Environmental Management Science Program Research in Massachusetts**

## **Massachusetts Institute of Technology, Plasma Science and Fusion Center**

### **81897 – Millimeter-Wave Measurements of High-Level and Low Activity Glass Melts**

**Principal Investigator:** Paul Woskov

**Problem Area:** High-Level Waste

Maximizing waste glass loading, optimizing durability of long-stability glass, and reducing long-term storage volumes are important needs of the Department of Energy/Environmental Management (DOE/EM) effort to help minimize nuclear clean up costs. The objectives of the proposed research make a focused contribution to these needs with a multi-organizational team, which includes an end user involved in current melter operations and development of next generation melters. The priorities of the proposed research are also guided by the Tanks Focus Area (TFA) with which the project team maintains close contact.

The research will continue development of real-time sensors for characterizing glass melts in high-level waste (HLW) and low activity waste (LAW) melters and to understand the scientific basis and bridge the gap between glass melt model data and melter performance. Millimeter-wave technology has been developed and tested for the measurement of temperature, viscosity, and density, and shows promise for conductivity and phase transitions (for example, liquidus temperature) measurements. Robust waveguide interfacing with the melter has made possible non-contact surface temperature profile measurements and internal melt measurements by waveguide immersion. Consequently, a significant advance is being achieved in the *in situ* capability and reliability of real-time monitoring of glass properties inside HLW and LAW melters.

New studies will be undertaken to expand the on-line glass property measurements for several waste glass chemistries of Savannah River Site (SRS), Idaho National Environmental Engineering Laboratory (INEL), and Hanford at Pacific Northwest National Laboratory. These new studies will support the development of new millimeter-wave monitoring capabilities such as the liquidus temperature and will enhance the understanding of the relationship between melt chemistry and millimeter-wave measurable characteristics. The work is closely tied to the needs of the Defense Waste processing Facility (DWPF) at SRS, West Valley Demonstration Project (WVDP), and vitrification efforts at Hanford, Oak Ridge, and Idaho sites. As an example of this tie and at the request of the TFA, a pilot test of a millimeter-wave pyrometer has been successfully performed on a real melter for two-dimensional surface temperature profile measurements for different cold cap coverage and processing conditions. To continue gaining acceptance of the millimeter wave technology as a tool by the TFA, additional viscosity and other melter parameter measurement tests are needed and proposed.

The new millimeter-wave sensors, when fully developed, will decrease the uncertainty in current property models and allow for improved operation and control of melters including feedback control. This would result in significant cost savings to the EM nuclear waste clean up effort and a significant success for the Environmental Management Science Program (EMSP). There is also a spin off potential to the commercial glass manufacturing and metals refining industries. The proposed research will continue a successful collaboration between the MIT Plasma Science and Fusion Center (PSFC), the Pacific Northwest National Laboratory (PNNL), and the Savannah River Technology Center (SRTC).

## **Annual Progress Reports**

### **2002 Progress Report**

# **Environmental Management Science Program Research in Idaho**

## **Idaho National Engineering and Environmental Laboratory**

### **81898 – Increasing Safety and Reducing Environmental Damage Risk from Aging High-Level Radioactive Waste Tanks**

**Principal Investigator:** Walter G. Reuter

**Problem Area:** High-Level Waste

The EMSP call identifies “a paramount need for improved understanding and modeling of the degradation mechanisms” of high-level waste containers. Responding to this need, we propose to develop and verify models of degradation due to cracks in containment tanks, based on extending fracture mechanics methodologies. While studies in fracture mechanics have advanced, materials investigated to date have limited ductility, so these theories cannot be applied to the tank materials, either at INEEL, Savannah River, or Hanford without further research. In particular, there are serious limitations to current theories regarding growth of surface cracks through the thickness, and extended growth of through-thickness cracks.

The achievements sought using innovative research are:

1. Develop slip line fracture mechanics (SLFM, a new ductile fracture modeling methodology) with the goal of predicting growth of surface cracks to the point of penetration of the opposing surface;
2. Quantify the stress and displacement fields surrounding a growing crack front (slanted and tunneled) under generalized plane stress conditions using fully plastic, three-dimensional Finite Element Method (FEM) analysis; and
3. Quantify the fracture process associated with the transition of stable ductile crack growth to unstable cleavage fracture, including estimates of event probability.

These objectives build the groundwork for a reliable predictive model of fracture in the HLW storage tanks that is also applicable to the standardized spent nuclear fuel storage canisters. This predictive capability not only improves the safety of workers and the public and reduces the potential for severe environmental damage, it also can extend the design life of the structures.

## **Annual Progress Reports**

### **2002 Progress Report**

# **Environmental Management Science Program Research in Washington**

## **Pacific Northwest National Laboratory**

### **81908 – Origins of Deviations from Transition-State Theory: Formulating a New Kinetic Rate Law for Dissolution of Silicates**

**Principal Investigator:** J. P. Icenhower

**Problem Area:** High-Level Waste

Contaminant release and migration models that are used to study a broad range of geochemical and environmental science problems commonly employ Transition-State Theory (TST) to regulate the dissolution kinetics of waste forms and minerals. Despite their widespread use in sophisticated reaction-transport codes, recent experiments have revealed that models based upon TST arguments are inaccurate when modeling solutions that contain high concentrations of dissolved components. Because solutions in subsurface environments are typically near saturation, TST-based predictions are questionable, and so may be remediation schemes that stem from these projections. Overly conservative and costly designs for high- and low-level waste disposal sites, and remediation strategies for plume migration will, therefore, have to be pursued to circumvent errors. In this proposal, we will develop and validate a new rate law that more accurately predicts dissolution kinetics in realistic solution compositions. The reactivity of borosilicate glass, synthetic plagioclase feldspar, and biotite will be determined over a range of solution saturation values. Because the solutions will be doped in the same elements that comprise the solids, the solid phases will be doped with radioactive tracers. To determine the control of element release in near-saturated solutions on defect populations, we will use atomic force microscopy and vertical scanning interferometry to compare rates of natural and synthetic feldspar and biotite. Surface species will be quantified using specular reflectance and photoacoustic FTIR methods. From these data we will be able to identify the reactive precursor species that are the key to unraveling rate mechanisms. The resulting model will have widespread application to geochemistry problems and will form the foundation of sound prediction.

### **Annual Progress Reports**

#### **2002 Progress Report**

# **Environmental Management Science Program Research in Washington**

## **Pacific Northwest National Laboratory**

### **81912 – Electroactive Materials for Anion Separation – Technetium from Nitrate**

**Principal Investigator:** Johanes H. Sukamto

**Problem Area:** High-Level Waste

The proposed research will provide the basis for using electroactive ion exchange materials to remove anionic contaminants from HLW wastes and process streams. An ion exchange process using electroactive materials sorbs contaminants selectively and then expels (elutes) them electrochemically by changing the charge balance through redox reactions in the sorbent as opposed to requiring the addition of a chemical eluant. Such processes can theoretically remove anions (e.g., pertechnetate, chromate) and concentrate them in a separate product stream while adding no process chemicals. A practical implementation in HLW process facilities would be a breakthrough in the ability of DOE to economically minimize waste and prevent pollution throughout the complex. To enable this, our work focuses on manipulating specific properties of redox polymers to control the hydrophobicity and ion-pair properties pertinent to the reversibility, selectivity, stability, intercalation/de-intercalation rates, and capacity of the polymers. This involves determining and controlling the density of charged sites, mobility of charged sites, degree of cross-linking, functionality of side groups and polymer chain length. The work will be performed by: Pacific Northwest National Laboratory (synthesis and characterization of polymers); Brookhaven National Laboratory (direct characterization of ion-pair interactions); University of Minnesota (synthesis and characterization of high capacity polymers).

### **Annual Progress Reports**

#### **2002 Progress Report**

# **Environmental Management Science Program Research in Washington**

## **Pacific Northwest National Laboratory**

### **81921 – Technetium Chemistry in HLW: Role of Organic Complexants**

**Principal Investigator:** Dr. Nancy J. Hess

**Problem Area:** High-Level Waste

The premise of the proposed research is that technetium (Tc) complexation with organic compounds in tank waste plays a significant role in the redox chemistry of Tc and the partitioning of Tc between the supernatant and sludge components in waste tanks. These processes need to be understood so that strategies to effectively remove Tc from high-level nuclear waste prior to waste immobilization can be developed and so that long-term consequences of Tc remaining in residual waste after sludge removal can be evaluated. Unfortunately, there is only limited data on the stability of Tc-organic complexes and even less thermodynamic data on which to develop predictive models of Tc chemical behavior. To meet these challenges we present a research program to study Tc-speciation in actual tank waste using state-of-the-art analytical organic chemistry, separations, and speciation techniques. On the basis of such studies we will acquire thermodynamic data for the identified Tc-organic complexes over a wide range of chemical conditions in order to develop credible models to predict Tc speciation in tank waste and Tc behavior during waste pretreatment processing and in waste tank residuals.

### **Annual Progress Reports**

#### **2002 Progress Report**

# **Environmental Management Science Program Research in Washington**

## **Pacific Northwest National Laboratory**

### **81923 – Radioanalytical Chemistry for Automated Nuclear Waste Process Monitoring**

**Principal Investigator:** Dr. Oleg Egorov

**Problem Area:** High-Level Waste

We propose a research program directed toward rapid, sensitive, and selective determination of beta- and alpha-emitting radionuclides such as  $^{99}\text{Tc}$ ,  $^{90}\text{Sr}$ , and trans-uranium (TRU) elements in low activity waste (LAW) processing streams. Nuclear waste process streams are particularly challenging due to the complex, high-ionic-strength, caustic brine sample matrix, the presence of interfering radionuclides, and the sometimes variable and uncertain speciation of the radionuclides to be analyzed. As a result, matrix modification, speciation control, and separation chemistries are required for use in automated process analyzers. Significant knowledge gaps exist relative to designing chemistries for such analyzers so that radionuclides can be quantitatively and rapidly separated and analyzed in high ionic strength solutions derived from low activity waste processing operations. These knowledge gaps will be addressed in this proposal and automated microscale fluid handling techniques will be used to integrate sample modification, chemical separation chemistries, and radiometric detection steps within a single functional process analytical instrument.

The outcome of these investigations will be the knowledge necessary to choose appropriate chemistries for sample matrix modification and analyte speciation control and chemistries for rapid and selective separation and preconcentration of target radionuclides from complex sample matrices. In addition, new approaches for quantification of alpha emitters in solution using solid state diode detectors, and improved instrumentation and signal processing techniques for use with solid state and scintillation detectors, will be developed. New knowledge of the performance of separation materials, matrix modification and speciation control chemistries, instrument configurations, and quantitative analytical approaches will provide the basis for designing effective instrumentation for radioanalytical process monitoring.

### **Annual Progress Reports**

#### **2002 Progress Report**



## **Environmental Management Science Program Research in Tennessee**

### **Oak Ridge National Laboratory**

#### **81924 – Optical and Microcantilever-Based Sensors for Real-Time In Situ Characterization of High-Level Waste**

**Principal Investigator:** Gilbert M. Brown

**Problem Area:** High-Level Waste

Fundamental research will be conducted to develop sensors for strontium that can be used in real-time to characterize high-level waste (HLW) process streams. Two fundamentally different approaches will be pursued, which have in common the dependence on highly selective molecular recognition agents. In one approach, an array of chemically selective sensors with sensitive fluorescent probes to signal the presence of the constituent of interest will be coupled to fiber optics for remote analytical applications. The second approach will employ sensitive microcantilever sensors that have been demonstrated to have unprecedented sensitivity in solution for  $\text{Cs}^+$  and  $\text{CrO}_4^-$ . Selectivity in microcantilever-based sensors is achieved by modifying the surface of a gold coated cantilever with a monolayer coating of an alkane thiol derivative of the molecular recognition agent. The approaches are complementary since fiber optic sensors can be deployed in the highly alkaline environment of HLW, but a method of immobilizing a fluorescent molecular recognition agents in a polymer film or bead on the surface of the optical fiber has yet to be demonstrated. The microcantilever-based sensors function by converting molecular complexation into surface stress, and they have been demonstrated to have the requisite sensitivity. However, fundamental research will be needed to devise a method of employing Si or SiC microcantilever sensors in the highly alkaline environment of HLW while maintaining high selectivity. Fundamental research is needed to develop Sr(II) molecular recognition agents with rapidly established equilibria needed for real-time analysis, and initial research will focus on calixarene-crown ethers as a platform. Sensors for alkali metal ions, hydroxide, and temperature will be part of the array of sensor elements that are demonstrated in this program for both the cantilever and fiber optic approaches.

### **Annual Progress Reports**

#### **2002 Progress Report**

# Environmental Management Science Program Research in Tennessee

## Oak Ridge National Laboratory

### 81926 – Chemistry of Actinides in Molten Glasses and Its Correlation to Structural Performance of Solid Glasses: Filling the Knowledge Gap

**Principal Investigator:** Sheng Dai

**Problem Area:** High-Level Waste

Borosilicate glasses are the primary matrixes used in the immobilization of high-level nuclear wastes. Although there are several prior EMSP research programs targeted for understanding solid behaviors of borosilicate matrixes, *no research* has been initiated to understand the chemistry of *molten* glasses. Chemical processes occurring in molten glasses are key elements in determining efficient immobilization and the long term stability of glasses. Confidence and assurance that long-term immobilization will be successful warrants research and improved understanding of the structural and thermodynamic properties of molten glasses. Today there are new opportunities to apply our recent developments in high-temperature spectroscopy techniques, not just to make concentration determinations in molten glasses, but indeed as *tools* to study radionuclide chemistry that occurs in molten glasses. We can draw upon our extensive and unique expertise from past and present research programs on high temperature molten salt chemistry to address this complex area, which could open new avenues for the design of efficient vitrification processes. The underlying goal of the proposed research is to make use of our high-temperature spectroscopic techniques to increase our fundamental understanding of the vitrification processes. In particular, we propose to study the relationship between the chemistry of molten glasses and the structural features of final solid glasses. The fundamental knowledge gained in this study will fill a crucial knowledge gap concerning chemistry of actinides in molten glasses and have a broad impact on the design and construction of advanced vitrification processes. This proposal specifically addresses needs for (a) fundamental chemical studies of actinides in molten glasses, (b) the determination of radionuclide species concentration in molten glass solutions, and (c) a predictive theory of actinide-doped glasses. Fundamental studies are proposed which are directed at characterizing and identifying *in-situ* actinide species formed in borosilicate glasses used in high-level waste (HLW) immobilization as a function of the composition of the glass, melt processing parameters and final state of the amorphous material. The ultimate goal of these investigations is to understand, at the atomic level, the chemistry of actinides in glass-forming melts and to use this understanding to evaluate current immobilization processes as well as help in the design of new systems. High temperature UV/Vis and near-IR spectral data will be used to investigate the solubility of actinide species in various molten glasses as a function of the composition and temperature. These data will be used to develop a new “optical basicity” scale for actinide stability and speciation in oxide glasses in analogy to the common pH scale used to define the acid-base properties of aqueous systems. Fluorescence lifetime distribution methods, fluorescence line-narrowing spectroscopy and x-ray absorption spectroscopy (XAS) will provide information on the local environment of the actinides while EPR and x-ray absorption edge positions will be used to define the oxidation states of actinide species in glasses. The combination of the optical basicity scale and structural information from fluorescence and XAS investigations, will be used to produce a detailed description of the identities and behavior of actinide species in silicate-based glasses. This stability model will be correlated to actinide leaching behavior for a glass matrix and offers a simple but powerful set of spectral “fingerprints” to predict the behavior of actinide species when immobilized in a glass. Four principal sets of results are expected from this research:

- (1) understand the solubilities and redox chemistry of actinides in *molten glasses*;
- (2) develop a *molecular description* for the immobilization process;
- (3) develop a new “*optical pH*” scale relating actinide complex identity to the composition and oxidic character of a glass;
- (4) correlate key spectral *fingerprints* to leaching rates and stabilities of actinides species in glass matrices.

## Annual Progress Reports

### 2002 Progress Report

# Environmental Management Science Program Research in Tennessee

## Oak Ridge National Laboratory

### 81927 – A New Method for In-situ Characterization of Important Actinides and Technetium Compounds via Fiberoptic Surface Enhanced Raman Spectroscopy (SERS)

**Principal Investigator:** Sheng Dai

**Problem Area:** High-Level Waste

In-situ characterization of actinides and technetium compounds in high-level wastes is essential to achieve shorter turn-around times for analytical results or to facilitate tank closure after retrieval. Currently, techniques for monitoring and characterizing radionuclides rely primarily on liquid scintillation counting, ICP-MS, and some limited use of the spectrofluorimetry based on fluorescence of radionuclide species under laser or UV excitation. These techniques require chemical handling, e.g., the use of complexing media, scintillation cocktails, phosphoric acids, in order to enhance signals. Furthermore, only fluorescent radionuclides ( $\text{UO}_2^{2+}$ ,  $\text{Cm(III)}$ ,  $\text{Am(III)}$ ) can be detected by the last technique. Many environmentally-important radionuclides such as plutonium, neptunium, and technetium species have no strong fluorescence signals and therefore can not be characterized via fluorescence spectroscopy.

This proposed research serves to fill this information gap through the development of a novel surface-enhanced Raman scattering (SERS) spectroscopy to selectively and sensitively monitor and characterize the chemical speciation of radionuclides at trace levels. The SERS technique permits both of these measurements to be made simultaneously, and results in significant improvement over current methods in reducing time of analysis, cost, and sample manipulation. Our overall goal is (a) to develop a scientific basis for this new methodology to detect radionuclides via SERS; and (b) to rationally synthesize and evaluate novel sol-gel based SERS substrates tailored to sensitively detect and characterize inorganic radionuclides such as  $\text{TcO}_4^-$ , actinyl ions (e.g.,  $\text{UO}_2^{2+}$ ,  $\text{NpO}_2^+$ , and  $\text{PuO}_2^{2+}$ ) and other chemical compounds of interest in subsurface environments and groundwater. This research will build on ORNL's recent demonstration of SERS for  $\text{UO}_2^{2+}$  and  $\text{TcO}_4^-$ ; that uses our newly-developed silver sol-gel film. Our original work has attracted world-wide interests in the sensitive and selective actinide detection and characterization research. Both French and Japanese researchers in this area have verified our preliminary results and detected uranyl concentrations as low as  $10^{-9}$  M. A combinatorial chemistry approach will be used to search for new and better SERS substrates, and we will incorporate molecular recognition components within these films to further improve selectivity and sensitivity. The rational design of our "smart" SERS substrates is based on a novel sol-gel process. The unique features of the sol-gel fabrication of SERS substrates will allow (a) a combinatorial search for optimum SERS substrates by the variation of a multitude of sol-gel preparation parameters; and (b) incorporation of molecular recognition via grafting functional groups into our matrices or co-doping other chemicals along with metal particles to further enhance substrate adsorption affinities toward target molecules. Four principal sets of results are expected from this research:

- A new and highly-sensitive methodology for radionuclide monitoring and characterization at the molecular level will be developed via SERS. No inherent chemical handling, such as the addition of chelating agents, is required in this method.
- Structural information concerning speciation and chemical states of important radionuclides (e.g.,  $\text{TcO}_4^-$ ,  $\text{UO}_2^{2+}$ ,  $\text{NpO}_2^+$ , and  $\text{PuO}_2^{2+}$ ) obtained via SERS will provide essential information to cost-effectively remediate and separate the radionuclides from contaminated media.
- This research will lead to a new generation of SERS substrates and a combinatorial chemical methodology for developing and evaluating chemical sensors.
- The interface of our SERS substrates with fiberoptic instrumentation for remote *in-situ* sensing will be conducted to gain understanding of speciation of radionuclides under real environmental conditions.

## Annual Progress Reports

### 2002 Progress Report

# Environmental Management Science Program Research in Tennessee

## Oak Ridge National Laboratory

### 81929 – Novel Fission-Product Separation Based on Room-Temperature Ionic Liquids

**Principal Investigator:** Huimin Luo

**Problem Area:** High-Level Waste

DOE's underground storage tanks at Hanford, Savannah River Site (SRS), and Idaho National Environmental Engineering Laboratory (INEEL) contain liquid wastes with high concentrations of radioactive cesium-137. Since the primary chemical components of alkaline supernatants are sodium nitrate and sodium hydroxide, the majority of the waste could be disposed of as low level waste and it would cost significantly less to treat the rest of the waste if cesium-137 and strontium-90 could be selectively removed. The above need to efficiently separate cesium-137 and strontium-90 from high-level wastes is also specified in High-Level Waste Science Needs (<http://emsp.em.doe.gov/focus> and EMSP Call LAB 01-16). The underlying goal of the proposed research is to develop a new solvent extraction process for separation of cesium-137 and strontium-90 from tank wastes based on ionic liquids. Ionic liquids are attracting increased attention world-wide because they promise significant environmental benefits. They are easy to recycle, nonflammable, chemically tunable, and have no detectable vapor pressure. These unique superior attributes make them "designer solvents" as potential replacements for noxious volatile organic compounds, which can contribute to air pollution and health problems for process workers. Our research will build on our recent preliminary demonstrations that  $\text{Sr}^{2+}$  and  $\text{Cs}^+$  can be selectively extracted from aqueous solutions into ionic liquids using crown ethers and unprecedented large distribution coefficients can be achieved for these fission products. Whereas conventional solvent extraction of  $\text{Sr}^{2+}$  and  $\text{Cs}^+$  using crown ethers and related extractants can deliver practical  $D_M$  value of up to two orders of magnitude ( $10^2$ ), preliminary tests with ionic liquids as extraction solvents delivered values of  $D_M$  on the order of  $10^4$ . These results clearly show the enormous potential that ionic liquids possess for increasing the extractive strength of ionophores such as crown ethers in fission-product separation applications. The volume of secondary wastes will be significantly minimized in this new separation technology. Our specific goals are (a) to synthesize new *ionic liquids* tailored for the extractive separation of  $\text{Cs}^+$  and  $\text{Sr}^{2+}$ ; (b) to select optimum macrocyclic extractants through studies of complexation of fission products with macrocyclic extractants and transport in new extraction systems based on ionic liquids; (c) to develop efficient processes to recycle ionic liquids and crown ethers; (d) to investigate chemical stabilities of ionic liquids under strong acid, strong base, and high-level radiation conditions. We believe that this new separation approach will lead to the discovery and development of a new and very versatile class of solvent systems targeted for the separation of important fission products from high-level tank wastes.

A collaboration between established groups at Oak Ridge National Laboratory (ORNL), the University of Alabama, and the University of Mississippi combines the synthesis expertise with the solvent extraction and characterization expertises. The partner laboratories have well recognized programs in the area of ionic liquids, solvent extraction using crown ethers, and physical chemistry involved in novel separations. Their cooperation under this research represents an unusual and extremely effective combination of unique resources. Basic research will focus on new recognition and separation principles applicable to fission products in ionic liquids. The new separation technology developed in this work will lead to a significant advance in the efficiency of cesium extraction from high-level waste, thereby greatly reducing energy usage and air pollution.

## Annual Progress Reports

### 2002 Progress Report

# **Environmental Management Science Program Research in Tennessee**

## **Oak Ridge National Laboratory**

### **81934 – Stability of High-Level Radioactive Waste Forms**

**Principal Investigator:** Theodore M. Besmann

**Problem Area:** High-Level Waste

High-level waste (HLW) glass compositions, processing schemes, limits on waste loading, and corrosion/dissolution release models are dependent on an accurate knowledge of liquidus temperatures and thermochemical values. Unfortunately, existing models for the liquidus are empirically-based, depending on extrapolations of experimental information. In addition, present models of leaching behavior of glass waste forms use simplistic assumptions of the thermochemistry or experimentally measured values obtained under non-realistic conditions. There is thus a critical need for both more accurate and more widely applicable models for HLW glass behavior.

In the previous project significant progress was made in modeling HLW glass. Borosilicate glass was accurately represented along with the additional  $\text{FeO-Fe}_2\text{O}_3$ ,  $\text{Li}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{MgO}$ , and  $\text{CaO}$  components. Nepheline precipitation, an issue in Hanford HLW formulations, was modeled and shown to be predictive. The objective of the proposed new effort is to continue the development of a basic understanding of the phase equilibria and solid solution of HLW glasses, incorporating other critical waste constituents including, S, Cr, F, P, actinides and rare earths. With regard to a fundamental understanding of solution oxides, there should be added insights on defect chemistry, interstitial behavior, clustering, and the energetics of metal oxide solutes.

## **Annual Progress Reports**

### **2002 Progress Report**

## **Environmental Management Science Program Research in Tennessee**

### **Oak Ridge National Laboratory**

#### **81935 – Ion Recognition Approach to Volume Reduction of Alkaline Tank Waste by Separation of Sodium Salts**

**Principal Investigator:** Bruce A. Moyer

**Problem Area:** High-Level Waste

In this renewal proposal, a 3-year collaborative project involving Oak Ridge National Laboratory, Pacific Northwest National Laboratory (G. J. Lumetta), and the University of North Texas (Prof. A.P. Marchand) is proposed to explore new approaches to the separation of sodium hydroxide, sodium nitrate, and other sodium salts from high-level alkaline tank waste. The principal potential benefit of this research is a major reduction in the volume of the high-activity waste stream, obviating the building of expensive new waste tanks and reducing the costs of vitrification. Principles of ion recognition will be researched toward discovery of liquid-liquid extraction systems that selectively separate sodium hydroxide and nitrate from waste-like matrices. Successful approaches to sodium hydroxide separation that were discovered in the prior three years will be enhanced by further efforts to understand the underlying properties of the controlling equilibria. This work will employ the novel concept of pseudo hydroxide extraction by fluorinated alcohols and phenols that function by cation exchange at elevated pH values. Crown ethers designed for sodium binding will be examined as possible synergists, and new ionizable lariat ethers will be synthesized as a new class of pseudo hydroxide extractants (UNT). A new thrust will be initiated to specifically target sodium nitrate. Applicable principles to be understood include solvation effects that promote efficient sodium nitrate extraction and appropriate crown ether design for efficient sodium binding and rejection of cesium. A proposed approach to the combined removal of sodium salts will be examined. Studies with real tank waste at PNNL will provide feedback toward solvent designs that have desirable properties.

### **Annual Progress Reports**

#### **2002 Progress Report**

## **Environmental Management Science Program Research in Tennessee**

### **Oak Ridge National Laboratory**

#### **81936 – Combined Extraction of Cesium, Strontium, and Actinides for Alkaline Media: An Extension of the Caustic-Side Solvent Extraction (CSSX) Process Technology**

**Principal Investigator:** Laetitia H. Delmau

**Problem Area:** High-Level Waste

Fundamental research on combined cesium, strontium, and actinide separation from alkaline media by solvent extraction is proposed, to address the EM problem area of the need for more efficient processes for the combined separation of these elements. Solvent extraction using the calixarene-based CSSX process has been shown to be a very effective separation method for cesium removal from High-Level Waste (HLW) present at the U.S. Department of Energy's (U.S. DOE's) Savannah River Site. We propose to study the extension of this technology to the extraction of strontium and actinides from caustic matrices, using a combination of selective, possibly synergistic, ligands. Specific extractants for actinides and strontium from alkaline media will be synthesized to investigate the feasibility of selective removal of these elements. Fundamental studies will be conducted to characterize their physical properties and extraction behavior from a wide variety of alkaline conditions. This extension of solvent extraction systems will be studied from a fundamental perspective to explore the option of combined or sequential processes. Such high efficiency separation systems would decrease the footprint of the process facility and minimize secondary waste volume compared to the current technology.

### **Annual Progress Reports**

#### **2002 Progress Report**

## **Environmental Management Science Program Research in Tennessee**

### **Oak Ridge National Laboratory**

#### **81939 – Hybrid Micro-Electro-Mechanical Systems (MEMS) for Highly Reliable and Selective Characterization of Tank Waste**

**Principal Investigator:** Panos Datskos

**Problem Area:** High-Level Waste

Innovative technologies of sensitive and selective chemical monitoring of hazardous wastes are of continuing importance to the environmental program of DOE. A multifaceted research program aimed at the fundamental and practical development of hybrid micro-electro-mechanical-systems (MEMS) that integrate several elements of chemical selectivity and sensor function is proposed. We will develop MEMS sensors that combine chemi-mechanical transduction, electrochemical (EC) detection, surface enhanced Raman spectroscopy (SERS), and radiation detection.

Based on our prior EMSP-supported research, we have developed highly effective methods of immobilizing a wide variety of molecular and ionic recognition phases onto micromechanical surfaces. These phases have been shown to provide efficient chemi-mechanical transduction and generation of large mechanical responses caused by adsorption of targeted analytes. We have introduced fundamentally new modes of adsorbate-induced surface stress through nano-structuring of microcantilever surfaces; the responsivity for this approach has increased by over two-orders of magnitude over previously existing technological approaches. Noble metal nanostructures similar to those that enhance chemi-mechanical transduction exhibit substantial Raman enhancement factors are expected to have a great potential for EC detection.

The proposed research will build on these results and focus on reliable characterization of highly complex systems in aqueous (at-tank) environments. In particular, MEMS with noble metal nano-structures will be integrated into microfluidic systems that provide improved selectivity and structural elucidation afforded by electrochemical (EC) and surface enhanced Raman scattering (SERS) methods. Invoking optical probing of microcantilever bending, we aim to acquire quantitative information on the composition of aqueous systems with medium-to-high levels of selectivity.

The proposed studies will provide substantial advances in sensor technology that will find specific applicability in the characterization of tank wastes as well as broader impact in chemical analysis. The impact of the fundamental aspects of this work includes better understanding of molecular-level interfacial phenomena in the systems with nano-scale confinement.

**This project began in 2001. The first progress report is expected in late 2003.**



# **Environmental Management Science Program Research in Illinois**

## **Argonne National Laboratory**

### **81940 – Characterization of Actinides in Simulated Alkaline Tank Waste Sludges and Leach**

**Principal Investigator:** Dr. Kenneth L. Nash

**Problem Area:** High-Level Waste

Previous work on this project has examined the leaching behavior of actinides from simulants of tank waste sludges derived from the bismuth phosphate, Redox, and PUREX processes, the principal chemical separations processes that operated at Hanford for plutonium production. We also have conducted fundamental investigations of the speciation of uranium and neptunium in solutions representative of proposed alkaline sludge washing liquors. Ongoing research focuses on investigating the speciation of Np, U, and Pu in strongly alkaline solutions containing chelating agents that are known to be present in Hanford waste tanks. Correlation of results from sludge leaching indicate that, while Am and Pu are generally not appreciably dissolved in alkali, Np and U can be solubilized during alkaline sludge washing. Leaching of sludges with acidic solutions and strong complexing agents indicate considerable association of all actinide ions with Cr, Fe, and Mn oxides in the sludge simulants. Electrochemical experiments conducted in strongly alkaline solutions have defined the formal potentials of Np in strong base and reveal that mononuclear hydrolysis products dominate the speciation of neptunium (and by analogy U and Pu) in concentrated alkali. Sodium ions appear to retard actinide solubility in such media. To extend these results, additional research is needed; on the speciation of U, Np, and Pu in concentrated alkali with chelating agents present; on kinetic studies of dissolution/redeposition mechanisms; on the relationship between  $Al_2O_3$  dissolution conditions and actinide speciation; and on the potential impact of redox sludge scrubs (proposed to improve Cr removal) on actinide speciation in alkaline and acidic solutions.

## **Annual Progress Reports**

### **2002 Progress Report**

# **Environmental Management Science Program Research in South Carolina**

## **Savannah River Technology Center**

### **81949 – Strategic Design and Optimization of Inorganic Sorbents for Cesium, Strontium and Actinides**

**Principal Investigator:** Dr. David Hobbs

**Problem Area:** High-Level Waste

Cost effective disposal of the large quantities of high-level radioactive waste solutions that presently exist within the DOE complex requires reducing the radioactivity to the smallest possible volume for incorporation into durable long-term waste forms such as borosilicate glass. The specific goals of this study are to develop a firm understanding of the factors that control selectivity and kinetics and apply that understanding to the synthesis of a novel material that will optimally separate cesium, strontium and actinides from the waste solutions in which they presently exist. This study will focus on titanium-based inorganic materials and related metal oxides that behave as ion exchangers or sorbents when exposed to the fission products and actinides in the waste solutions produced from nuclear materials reprocessing.

Although these materials exhibit many of the desired properties, a complete understanding of their properties and the manner in which they function has not yet been achieved. Specific areas that require study in order to maximize the benefits of these materials include: their sorption or exchange mechanisms, the interactions between the sorbate and the exchanger, and the structural features dictating the kinetics and selectivity of the exchanger. With an understanding of these properties we can meet the immense challenges of designing materials with the correct selectivity in chemically demanding environments, adequate stability in extreme radiation fields and chemical media, and the exchange kinetics rapid enough to ensure safe, efficient, and thorough separation.

## **Annual Progress Reports**

### **2002 Progress Report**

# **Environmental Management Science Program Research in New Mexico**

## **Sandia National Laboratory**

### **81959 – A Comprehensive Study of the Solubility, Thermochemistry, Ion Exchange, and Precipitation Kinetics of NO<sub>3</sub> Sodalite**

**Principal Investigator:** Carlos Jove

**Problem Area:** High-Level Waste

Zeolitic sodium aluminosilicates have been found to interfere with a number of processes intended to empty high-level nuclear waste tanks and process their contents. They are prime constituents of resilient heels observed on the bottom of Savannah River tanks. This same material also has fouled a high-level waste (HLW) evaporator, necessitating construction of a \$ 50,000,000 replacement unit. Entrained in the fouled evaporator scale is close to a critical mass of enriched uranium, so remediating this facility is the second substantial cost associated with the precipitation of these materials. In addition, these compounds have also been implicated as interfering with Cs recovery operations during waste treatment processes and may provide radionuclide sinks in a variety of locations of great environmental sensitivity. These are just the main problems to be encountered to date and only a small fraction of the nation's HLW has been processed. Clearly, a better understanding of the factors governing the occurrence and possible removal of these zeolitic materials would be a timely contribution to the DOE arsenal for dealing with its HLW remediation problems.

The proposed research takes an integrated approach to obtaining a basic understanding of these materials. A thermodynamic analysis is the key to understanding when and where these materials will precipitate from the great variety of fluids found around the DOE Complex. To obtain this we anticipate: (1) performing a comprehensive body of solubility experiments designed to provide solubility products for the relevant materials, (2) calorimetric measurements to supplement (and verify) the thermodynamic constants deduced from the solubility studies. In addition, the proposed research contains an extensive NMR component intended to provide a mechanistic understanding of the precipitation mechanisms and to confirm the aqueous speciation of silica and alumina in the solutions from which these materials precipitate. Finally, a combined synthesis and nuclear magnetic resonance (NMR) study will be carried out to assess if radionuclides and Resource Conservation and Recovery Act (RCRA) metals might also be concentrated in a precipitate that, to date, has mostly proven problematic from the standpoint of causing mechanical problems.

## **Annual Progress Reports**

### **2002 Progress Report**

# **Environmental Management Science Program Research in Washington Washington State University**

## **81962 – Understanding the Chemistry of the Actinides in HLW Tank Systems**

**Principal Investigator:** Dr. Sue B. Clark

**Problem Area:** High-Level Waste

The remediation of DOE's HLW tanks is an enormously challenging problem. The waste is highly radioactive resulting from the large quantities of plutonium, actinides, and fission products. The chemical matrices of the various HLW tanks are extremely harsh, with pHs in excess of 14, elevated temperatures due to radiolytic heating and a wide array of organic ligands used in materials processing and their degradation products. To remove waste from the tanks, DOE must design strategies to characterize the material safely, separate the radioactivity (i.e., the fission products and actinides) from the large quantity of non-radioactive material, and immobilize the radioactive waste for geologic disposal.

The Tanks Focus Area (TFA) is currently using the Environmental Simulations Program (ESP) to simulate these chemical processes. The ESP relies on a thermodynamic database to make predictions on the chemical speciation of components in the waste, including the actinides. This requires that the chemistry of plutonium and the actinides in these systems be understood, and that relevant chemical equilibria be defined and stability constants and other thermodynamic parameters be quantified. Unfortunately, relatively little is known about the behavior of plutonium and the actinides in highly alkaline systems with elevated temperatures and where organics are present. A database that describes the chemical equilibria and the impact of temperature on them does not exist.

The overall goal of the proposed research is to provide a thermodynamic basis for describing actinide speciation over a range of tank-like conditions. These conditions include elevated temperature, elevated OH<sup>-</sup> concentrations, and in the presence of various organic ligands. In 1998, we began research in this area under the EMSP program, and we have made significant progress as described in this proposal. However, considerable work remains to accomplish this goal. The objectives of this research plan are to:

1. Provide an experimental basis for describing actinide speciation over ranges of pH, temperature, and organic ligands relevant to HLW.
2. Use the information obtained from limited experimental work to develop a thermodynamic database predicting Pu/actinide speciation under wide ranges of conditions relevant to HLW. This will allow the extension of the ESP to simulate actinide chemistry in HLW and pretreatment processes.

The proposed work will be completed by a team of chemists and geochemists from Washington State University (WSU), University of Idaho (UI), Lawrence Berkeley National Lab (LBNL), and Pacific Northwest National Lab (PNNL). All of the collaborating partners have experience in actinide chemistry, solution chemistry, and thermodynamic modeling. The proposed research builds on the foundation of data generated in our current EMSP research program. The experimental work proposed will be completed by WSU, UI, and LBNL. We will work with Andy Felmy of PNNL to use the data we generate from our experimental work to create a thermodynamic database for the ESP and the TFA.

**This project began in 2001. The first progress report is expected in late 2003.**

# **Environmental Management Science Program Research in Pennsylvania**

## **The Pennsylvania State University**

### **81963 – Physical, Chemical and Structural Evolution of Zeolite-Containing Waste Forms Produced from Metakaolinite and Calcined Sodium Bearing Waste (HLW and/or LLW)**

**Principal Investigator:** M. Grutzeck

**Problem Area:** High-Level Waste

Liquid sodium bearing waste (SBW) can be calcined and solidified using metakaolinite and a limited amount of water. The processing does not require expensive specialized equipment or exotic materials but rather it can be done using conventional cement and/or concrete mixing equipment. The final product is cured at relatively low temperatures producing a dense ceramic-like material with strength in the 300-400 pounds per inch<sup>2</sup> (psi) range and leach rates comparable to glass waste forms with similar waste loading. This product is stable in realistic geologic settings due to the in situ growth of zeolites.

We have coined the term “hydroceramic” to describe these new waste forms. They have also been referred to as “hydroceramic cements” or “hydroceramic concretes” because of the similarity of the mixing and curing procedures used to make hydroceramics to those used when making cementitious materials. However, this is where the similarity ends because their chemistry is completely different. Hydroceramic waste forms attain their desirable characteristics from in situ formation of zeolites. The zeolitization process is a simple one. In processing hydroceramics, metakaolinite is mixed with calcined sodium-bearing waste and enough water to make a thick paste. The paste is transferred to a sealed metal canister and “soaked” for a few hours at 70-80°C prior to conventional oven heating or steam autoclaving at 90-180°C for varying periods of time. Once mixed and cured at elevated temperatures, these ingredients react to form a hard, dense, ceramic-like material that contains significant amounts of crystalline tectosilicates (zeolites and feldspathoids). Our data so far have shown that hydroceramics could well be a viable alternative for fixation of low activity sodium bearing waste. Our processing method includes pretreating the liquid waste, which maximizes the reactivity and composition of the resulting calcine. The objective of the continuation study is to further adapt this technology for use in site remediation and clean up of caustic waste solutions now in storage in tanks at Hanford and the Savannah River sites. The proposed work is meant to develop a clearer understanding of the advantages and limitations of producing a zeolite-containing hydroceramic from the low activity SBW at these sites, i.e., the effect of processing variables, reaction kinetics, crystal and phase chemistry, and microstructure on the performance of the waste form. In addition, we are proposing to further refine our processing to increase waste loading in the hydroceramics. It is our goal to not only refine our processing methodology but also to make the calcine fit the zeolitization process as best as possible. It’s not surprising that the encapsulation of these liquid sodium bearing waste involves complex chemistry. We have already successfully produced hydroceramics with sufficient strength and very low leach rate. It is proposed that by tailoring the calcination process, it will be possible to encapsulate many more radionuclides without sacrificing the performance of the waste form and thereby creating a better hydroceramic waste form.

**This project began in 2001. The first progress report is expected in late 2003.**

# **Environmental Management Science Program Research in Washington**

**University of Washington**

## **81964 – Physical Characterization of Solid-Liquid Slurries at High Weight Fractions Using Optical and Ultrasonic Methods**

**Principal Investigator:** Lloyd W. Burgess

**Problem Area:** High-Level Waste

Remediation of highly radioactive waste is a major technical and programmatic challenge for the DOE. Rapid, on-line physical characterization of highly concentrated slurries is required for the safe and efficient remediation of 90 million gallons of high-level radioactive waste (HLW), sodium bearing waste, and mixed waste remaining at five sites. This project develops a combination of innovative optical and ultrasonic measurement methodologies to provide this capability. This work provides the science base needed for the physical characterization of the HLW during pipeline transport and processing over wide ranges of particle size, shape, and composition in highly concentrated slurries. Near-surface characterization of the slurry flow in the particle size range from nanometer to micrometer will be realized by using optical low coherence reflectometry. Volumetric characterization at depths in the slurry flow up to several centimeters in the particle size range from the micrometer to millimeter will be realized by utilizing ultrasonic backscatter and diffuse fields. The proposed technology will also characterize and detect agglomeration and the onset of gelation during processing and pipeline transport.

One of the benefits of this combined approach is the physical characterization of HLW over a concentration and particle size range that is broader than can be achieved with today's technology. This will avoid a costly increase in waste stream volume due to excess dilution, and will lessen chance of plugging pipes that could shut down expensive processing lines. One of the strengths, the teaming up of significant talents in both experimental and theoretical optics (University of Washington) and in ultrasonics [Pacific Northwest National Laboratory (PNNL)] provides a synergistic approach to integrate these complimentary techniques.

The proposed approach has three elements: 1) the extension of optical and ultrasound interaction theories to consider multiple backscattering and diffuse fields in dense slurries; 2) experimental studies using optical and ultrasonic measurements on well characterized highly concentrated solid-liquid suspensions; and 3) the integration and application of optical and ultrasonic techniques, and inversion methodologies, applied to multi-component slurry simulants representative of stored waste. It should be noted, that the basic science developed during this project has implications for a wide range of applications to characterizing heterogeneous systems, such as those typically found in chemical and biological processing environments.

This proposed work will provide the fundamental science base needed to determine the physical properties of slurries at high concentrations over a wide range of particle sizes, by coupling optical and ultrasonic techniques. An innovative, novel characterization approach that couples optical and ultrasonic techniques will be developed. Specifically, this innovative approach will enable the physical characterization of slurries at high concentrations, thus avoiding costly excessive dilution. In addition, this work will provide a technology for monitoring slurry flow in pipes to avoid clogging due to sedimentation or gelation. This unique approach offers the best value for the DOE by providing techniques for characterizing the physical properties of HLW slurries during the entire remediation process.

## **Annual Progress Reports**

### **2002 Progress Report**

# **Environmental Management Science Program Research in New Mexico**

## **Los Alamos National Laboratory**

### **81967 – Radiochemical Analysis by High Sensitivity Dual-Optic Micro X-ray Fluorescence**

**Principal Investigator:** George J. Havrilla

**Problem Area:** High-Level Waste

Improved radiochemical analysis of high-level radioactive wastes at Savannah River Site and Hanford will be accomplished by a novel dual-optic micro X-ray fluorescence instrument. This innovative instrumental concept incorporates new X-ray optical elements such as monolithic polycapillaries and doubly bent crystals (DBC), which focus X-rays. The proposed approach uses either a polycapillary focusing optic or a DBC optic to provide a small and intense excitation X-ray beam. Both types of optics collect a large solid angle of X-rays from an X-ray tube and focus them to a small area, increasing the X-ray flux density on the sample by more than 1000 times over a conventional pinhole collimator. Another polycapillary optic will be used on the X-ray detection side as a spatial filter that only collects fluorescent X-rays from the area illuminated by the excitation X-rays. This will screen out the radiation background from the radioactive species in the specimen and significantly increase the detection sensitivity of the analysis. While the polycapillary optic transmits X-rays in a relatively wide energy range, the DBC optic provides monochromatic excitation, which eliminates the bremsstrahlung background from the X-ray source. This further reduces the background and improves the detection sensitivity. The choice of using the polycapillary optic or the DBC optic on the excitation side will depend on the application. The integration of these X-ray optics increases the signal-to-noise and thereby increases the sensitivity of the analysis for low-level analytes. This work will address a key need for radiochemical analysis of high-level waste using a non-destructive, multi-element, and rapid method in a radiation environment. There is significant potential that this instrumentation could be capable of on-line analysis for process waste stream characterization at these DOE sites.

## **Annual Progress Reports**

### **2002 Progress Report**

# Environmental Management Science Program Research in New Mexico

## Los Alamos National Laboratory

### 81988 – Identification of Non-Pertechnetate Species in Hanford Tank Waste, Their Synthesis, Characterization, and Fundamental Chemistry

**Principal Investigator:** Norman C. Schroeder

**Problem Area:** High-Level Waste

Technetium, as pertechnetate ( $\text{TcO}_4^-$ ), is a mobile species in the environment. This characteristic, along with its long half-life, ( $^{99}\text{Tc}$ ,  $t_{1/2} = 213,000$  a) makes technetium a major contributor to the long-term hazard associated with low level waste (LLW) disposal. Thus, technetium partitioning from nuclear waste tanks at DOE sites (Hanford, etc.) may be required so that the LLW forms meet DOE performance assessment criteria. Technetium separations assume that technetium exists as  $\text{TcO}_4^-$  in the tank waste. However, work with actual Hanford waste indicates that much of the technetium exists in a form other than  $\text{TcO}_4^-$  and that these unidentified technetium species are not readily converted to pertechnetate by oxidation.

Technetium was introduced into the tanks as the pertechnetate anion. However, years of thermal, chemical, and radiolytic digestion in the presence of organic material, including complexants such as ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), citrate, and oxalate, has transformed much of the  $\text{TcO}_4^-$  into stable, reduced, technetium complexes. To successfully partition technetium from tank wastes, it will be necessary to either remove these nonpertechnetate species with a new process, or reoxidize them to  $\text{TcO}_4^-$  so that a conventional pertechnetate separation scheme will be successful. The success of DOE's technetium management strategy lies in knowing what these non-pertechnetate species are and understanding their chemistry.

This research will use the technetium complexes prepared under our original EMSP proposal to develop a capillary electrophoresis mass spectrometry (CEMS) technique that will be used to identify non-pertechnetate species in actual waste samples. The model technetium complexes will be used as standards to establish the operational parameters for CEMS for the types of technetium compounds we speculate are in the waste. Development of this technique is even more critical to resolving the nonpertechnetate problem since many of the technetium complexes synthesized in our original proposal are too easily oxidized or show less stability in caustic media compared to the actual non-pertechnetate species in the waste.

This proposal has three major goals: (1) develop capillary electrophoresis mass spectrometry as a characterization technique, (2) separate a non-pertechnetate fraction from a waste sample and identify the non-pertechnetate species in it by CEMS, and (3) synthesize and characterize bulk quantities of the identified non-pertechnetate species and study their ligand substitution and redox chemistry.

The transition plan for this work would be to use the fundamental chemistry of the identified non-pertechnetate species to develop efficient oxidation or separation methods for the non-pertechnetate species in an actual waste matrix.

Meeting the major goals of this project and the transition plan would enable the development of separation and/or the feed adjustment chemistry that will efficiently remove technetium from the waste and enable DOE to fulfill its tank waste remediation mission.

## Annual Progress Reports

### 2002 Progress Report



# **Environmental Management Science Program Research in New Mexico**

## **Los Alamos National Laboratory**

### **81989 – The Influence of Radiation on Pit Solution Chemistry as it Pertains to the Transition from Metastable to Stable Pitting in Steels**

**Principal Investigator:** Dr. R. Scott Lillard

**Problem Area:** High-Level Waste

It has been recently demonstrated that the formation of stable, propagating, corrosion pits in steels is preceded by a series of metastable pitting events (often referred to as electrochemical noise). The kinetics of dissolution inside of these metastable pits (which are on the order of 0.1 microns in size) have been shown by this investigator, and others, to be controlled by lattice properties as well as the solution chemistry that develops in the incipient pit; due to hydrolysis reactions and restricted mass transport. These hydrolysis reactions, such as  $\text{Cr}^{+3} + 3\text{H}_2\text{O} \rightarrow \text{Cr}(\text{OH})_3 + 3\text{H}^+$  in the case of stainless steel, result in acidification and accelerate pit propagation rates. To successfully mitigate localized corrosion in carbon steel and stainless steel storage tanks, via inhibitors or material selection where possible, it is necessary to understand the influence of bulk solution chemistry (i.e., tank chemistry) and radiation on the hydrolysis and transport reactions inside the metastable pit as these parameters ultimately control the transition to stable pitting. For example,  $\text{Cr}^{+3}$  and  $\text{Fe}^{+2}$  are products of the stainless steel corrosion reaction inside the incipient pit. Their concentration controls the rate of acidification, which is one of the criteria for pit stabilization. However, both,  $\text{Cr}^{+3}$  or  $\text{Fe}^{+2}$  are water radiolysis scavengers. As the rate constants for scavenger reactions are fairly high it is anticipated that they will be depleted in the incipient pit during irradiation and, thus, may decrease the probability (in stainless steel) that a metastable will transition to stable pitting. Therefore, it is the goal of this proposal to understand the factors that influence the transition from metastable to stable pitting in the storage environment. Specifically, the influence of  $\gamma$ -radiation on local solution chemistry will be investigated.

To date, studies of pitting corrosion in radioactive waste environments have only provided anecdotal evidence of the pitting process. No direct correlation between observed phenomena and mechanism have been thus far made. This proposal combines seminal electrochemical methods for investigating metastable pitting activity during  $\gamma$ -irradiation with pit-solution analysis techniques to evaluate the role of solution chemistry in the stable pitting of steel waste storage tanks. To accomplish this, it will be necessary to characterize the relationships between radiation flux / radiation dose and metastable pitting frequency / magnitude. This will be accomplished with a  $^{60}\text{Co}$  source in our radiochemistry lab. In a set of separate experiments, we propose to use spectroscopic methods in combination with pulsed radiation sources (Febetron) to characterize the development of the local solution chemistry inside an artificial pit. The data from these experiments will be used in conjunction with the metastable pitting data and model predictions of pit solution development to determine the species that are both critical to the incipient pit chemistry and also participate in the water radiolysis scavenger reactions.

## **Annual Progress Reports**

### **2002 Progress Report**



## Environmental Management Science Program Research in Kansas

### University of Kansas

#### 54791 – Managing Tight Binding Receptors for New Separations Technologies

**Principal Investigator:** Dr. Daryle H. Busch

**Problem Area:** Mixed Waste

The overall purpose of the chemistry described here is to learn ways in which the most powerful ligands can be made useful in the service of separations science. Advantages of powerful ligands include: metal ions can be taken away from other reasonably strong binding sites, metal ions can be sequestered from very dilute media, and along with high affinity comes the possibility of high selectivity. Historically, the applications of such tight-binding ligands have been limited by the slow rates at which their equilibria are established. This program attacks this limitation in a most basic way, looking at means of facilitating both the binding and release processes, and considering a novel concept for a separations technology that is tolerant of slow equilibration. Three major objectives make up this research: (1) design of tight-binding ligands that can photo-release a metal ion, (2) investigate means for facilitating rapid binding by ligands with very high affinities for selected metal ions, and (3) develop template polymeric receptors that are imprinted for metal complexes of tight-binding ligands, but not for the free ligands. These investigations are motivated by the potential benefits that would derive from bringing extremely tight-binding ligands into separations processes.

#### Significance

The results sought in the studies would constitute major advances in the fundamental science of coordination chemistry, one of the foundations of separations science. Objective (1) extends the new science of photo-released reagents to metal ions, a development that maybe viewed as overdue. Fundamental questions regarding the photochemical reactions in this research include the following: (1) What will be the effects of the metal ion on the efficiency and, possibly, the nature of the photochemical reaction? (2) What will control the rate of release of the metal ion during the photochemical reaction? In a variety of applications, a metal ion may be firmly chelated until the demand for release is appropriate. At this point, photo release can applied and the metal ion is liberated for whatever role is intended. This could be a part of a separations process, an event in a chemical switching sequence (e.g., signaling the detection of light), the initiation of a metal ion catalyzed process. Thus the possible benefits of the proposed chemistry are wide ranging.

It is extremely important to understand the relationships between the thermodynamic (binding affinities) and kinetic (rates of binding and dissociation) properties of receptor/receptee interactions. This subject is addressed in our objective (2). The affinity of a complex is determined by the ratio of the rates of the binding and dissociation reactions, not the absolute values of those rate processes. Consequently, systems of vastly different labilities can, in principle, exhibit the same affinities. Accumulated knowledge suggests that lability tends to decline as affinity increases, hence the general realization that tight-binding receptors are too slow for traditional separations technologies. There are some hints in the literature of factors that

might permit acceleration of the binding process through molecular design. Clarification could lead to many applications because the range of applicable systems would, in many cases, be enhanced.

Objective (3) proposes to extend the varied studies on templated macroporous polymer receptors to the novel role of binding a selected tight-binding complex under conditions appropriate to important applications. These combined studies would also offer strong possibilities of applications and new technologies, or modified and improved technologies. Of particular interest to DOE is the application to the separation of metal ion contaminants from soils and dilute solutions.

Among the environmental pollution scenarios that are particularly troublesome to the standard separation and purification methodologies are (1) those involving extremely dilute streams of radioactive or RCRA elements and (2) those in which such substances are absorbed in soils. In both cases, tight-binding, adequately selective, receptors offer the possibility of effective new technologies. For case (1) large binding constants are essential because of the effect of the high dilution; i.e., the moderate affinities of the receptors used in traditional solvent extraction or ion exchange methodologies may not assure binding. In the case of pollutants in soils, chemical binding to soil components or the presence of mineral forms can offer strong competition to any but the strongest of competing receptors.

The methodology for using tight-binding ligands in contaminated soil remediation draws on an analogy with the ligands called siderophores that are secreted by certain bacteria in order to salvage iron from the soil. A very powerful ligand is excreted across the cell membrane into the soil. The ligand diffuses with the aid of moisture and dissolves iron from its mineral forms. The complex formed by the iron is then recognized by the membrane and drawn back into the cell. In our scenario, the selective tight-binding ligand of choice is sprayed into the irrigated soil in the presence of a templated macroporous polymer that has been imprinted for the complex of interest. The ligand binds the metal ion, and the complex diffuses to the polymer and is bound. The polymer beads are removed from the soil, either by flotation, magnetically, or some other physical means, and the metal ion is released from the polymer-bound ligand and converted to a concentrated waste form.

## **Annual Progress Reports**

**1997 Progress Report**

**1998 Progress Report**

**1999 Progress Report**

**2000 Progress Report**

# Environmental Management Science Program Research in Kansas

## University of Kansas

### 54864 – Supramolecular Chemistry of Selective Anion Recognition for Anions of Environmental Relevance

**Principal Investigator:** Dr. Kristen Bowman-James

**Problem Area:** Mixed Waste

The supramolecular chemistry of selective anion recognition by synthetic polyammonium macrocycles will be explored in a comprehensive, long term program designed to provide new solutions to problems critical to the environmental initiative of DOE. Highly shape- and charge selective systems will be designed, synthesized, and examined for their capabilities in sequestering environmentally important anions. Phase I of this program (years 1-3) will involve selected oxo anions: nitrate, phosphate, sulfate, chromate, and pertechnetate. Longer term initiatives will include expansion to other environmentally important anions as well as to other non-amine-based receptors. This project will involve major basic research components in the selection of target macrocycles using three areas to assess suitability. These areas are x-ray crystallographic structural determinations, molecular dynamics simulations, and thermodynamic and kinetic studies of anion binding. The results from this basic research component will be applied to environmental challenges including both sensing and separations of anions of interest.

**Part I.** The basic research components of this project consists of a three-pronged approach, chosen to probe the specifics of anion complexation and to provide a basic comprehensive understanding of anion/cation recognition and interaction.

*Solid state structural information* obtained by X-ray crystallographic techniques will be obtained to analyze the relationship between positive receptors and negative substrates for oxo anions of environmental interest.

*Molecular mechanics and molecular dynamics methodology* will be used to aid in the design of improved receptors with enhanced selectivities for anions of interest.

*Thermodynamic and kinetic parameters* will be used to gauge relative selectivities of the macrocycles for different substrates and will include the determination of protonation constants, complex formation constants, as well as entropies, enthalpies, and free energies of complexation.

**Part II.** The findings of the basic research component described above will be directed to the selection of receptors to be evaluated in more applied areas in sensor and separations chemistry. These studies will focus on three areas:

*The fabrication of anion selective electrodes* will be explored at the University of Kansas in our laboratories.

*Applications in liquid-liquid separations* will be explored in collaboration with Bruce Moyer at Oak Ridge National Laboratory.

*The reversible sequestration of heavy metal oxides* such a uranyl ion will be examined in collaboration with Paul Smith of Los Alamos National Laboratory. Our role in this project will be to provide appropriate receptors and a summer student to work at the Los Alamos Laboratory.

The results of this comprehensive program can potentially lead to superior systems for sensing and sequestration of anions of environmental importance, and therefore could have major impact on issues

involving hazardous waste sources, including Hanford underground tanks, groundwater, and process waste waters.

## **Annual Progress Reports**

**1997 Progress Report**

**1998 Progress Report**

**1999 Progress Report**

# Environmental Management Science Program Research in Washington

## University of Washington

### 60150 – Genetic Engineering of a Radiation-Resistant Bacterium for Biodegradation of Mixed Wastes

**Principal Investigator:** Dr. Mary E. Lidstrom

**Problem Area:** Mixed Waste

The mixture of toxic chemicals, heavy metals, halogenated solvents and radionuclides in many DOE waste materials presents a challenging problem for separating the different species and disposing of individual contaminants. One approach for dealing with mixed wastes would be to selectively remove classes of hazardous wastes from mixed waste streams, producing waste streams with less complex mixtures. Because of the initial chemical complexity of such mixtures, these treatment systems should be carried out at relatively low temperatures and pressures and without the addition of new chemicals, to avoid possible secondary reactions that might generate new toxic species. Therefore, a microbiological treatment system is an attractive possibility for separation and treatment. Systems are available in bacteria for detoxifying halogenated organics and toxic metals such as mercury, and theoretically these could be used to selectively remove these classes of compounds from mixed wastes. However, bacteria containing these systems would not be expected to survive in the mixed waste streams that must be treated. Recent work with the deinococci suggests a new approach of gamma-irradiation, and is also highly resistant to desiccation and to peroxides. This resistance is apparently due to highly active DNA repair systems, high chromosome copy number, and an unusual RecA protein. In addition, genetic systems now exist for this organism for cloning, genetic inactivation of chromosomal genes, and expression of foreign genes. Therefore, *D. radiodurans* is a candidate for a strain that could be genetically engineered to survive in and detoxify DOE's mixed waste streams.

In this project, it is proposed to develop a set of *D. radiodurans* strains specifically designed to survive in the toxic conditions found in DOE mixed waste streams. Genes from *E. coli*, *Shigella*, and *phage T4* have been stably expressed in *D. radiodurans*. Therefore, it should be possible to develop expression systems for foreign genes encoding biodegradative functions. In addition, the genome of *D. radiodurans* is currently being sequenced by TIGR, with projected completion and release in 1998. This database will be extremely useful for analyzing expression characteristics of genes and for identifying target genes for future genetic manipulation to increase resistance and optimize expression of foreign genes.

The first goal for this project will be to develop strains that are resistant to a number of toxic metals and that can detoxify a broad range of haloorganics. Specific aims are: 1) develop and optimize expression systems for *D. radiodurans*; 2) clone and express broad spectrum oxygenases that cometabolize haloorganics in *D. radiodurans*; 3) clone and express systems for heavy metal resistance and detoxification in *D. radiodurans*; and 4) test survival and degradation capacity of these strains in artificial mixtures of contaminants, designed to simulate DOE mixed waste streams. Such strains will then be candidates for developing treatment processes for mixed wastes by seeding with dried cells and using non-growth conditions.

## Annual Progress Reports

[1998 Progress Report](#)

[1999 Progress Report](#)

[2000 Progress Report](#)

# **Environmental Management Science Program Research in Maryland**

## **National Institute of Standards and Technology**

### **60231 – Novel Miniature Spectrometer for Remote Chemical Detection**

**Principal Investigator:** Dr. Andrew C. R. Pipino

**Problem Area:** Mixed Waste

This research will develop an entirely new class of chemical sensing technology that will enable qualitative and quantitative remote, real-time diagnostics of chemical species in hazardous gas, liquid, and semi-solid phases through a completely novel implementation of evanescent wave spectroscopy. The sensor design utilizes a small, solid block ( $< 1\text{cm}^3$ ) of ultra-high purity optical material that is fabricated into a regular, planar polygon with a convex facet to form a total-internal-reflection ring cavity. For light undergoing sustained circulation by total-internal-reflection inside the solid, the facets of the polygon act as extremely high-reflectivity (99.9999% in some cases) mirrors, resulting in a relatively long and accurately measurable lifetime for an injected light pulse. Evanescent waves, which are generated by total-internal-reflection, are absorbed by matter in the vicinity of the cavity where the evanescent wave decays exponentially in space. The absorption spectrum is extracted by measuring the mean lifetime of an injected light pulse as a function of pulse carrier frequency. Errors associated with light source fluctuations, which typically limit the sensitivity of conventional absorption methods, are eliminated by this single pulse measurement, as in the gas-phase technique known as cavity ring-down spectroscopy. By locating the light source and detection system at a distance (e.g., 0.1 to 10 Km) through the use of fiber-optics, this new technology will permit remote, high-sensitivity, broadband chemical sensing with a rugged, cost-effective, miniature spectrometer.

Preliminary studies indicate the feasibility and design considerations for this new class of devices. For the laboratory program the technical tasks include: 1) experiments that verify chemical sensitivity, 2) development of a fabrication strategy for ruggedly mounting the coupling prisms to the TIR-ring cavity, 3) design and fabrication of TIR-ring cavities that allow detection of chemical species in the near-and mid-infrared (IR) spectrum, 4) development of a fiber-optic interface to TIR-ring cavities, 5) characterization of the technology by using these devices to detect chemical species of importance to the EMSP mission, and 6) investigation of potential interferences, e.g., particulates, abrasives, inhomogeneities, temperature and density gradients.

## **Annual Progress Reports**

**1998 Progress Report**

**1999 Progress Report**

**2000 Progress Report**

# Environmental Management Science Program Research in Arizona

## University of Arizona

### 60326 – Isolation of Metals from Liquid Wastes: Reactive Scavenging in Turbulent Thermal Reactors

**Principal Investigator:** Dr. Jost O. L. Wendt

**Problem Area:** Mixed Waste

Metal-bearing liquids constitute a major part of the DOE waste inventory. This waste is extremely varied with respect to metals (radionuclides, heavy metals, transuranics) and other species (e.g., organics). For much of this waste, concentration of metals to reduce the volume requiring special isolation is critical. One potentially suitable technology is high-temperature reactive capture of volatile metals by readily available collectable particulate sorbents (kaolinite, bauxite, and limestone) injected downstream of a flame zone. High temperature reaction between metal vapor and sorbent forms environmentally benign products that are water unextractable.

We propose to begin developing the fundamental science base for understanding and evaluating a class of processes applicable to a broad range of aqueous and nonaqueous feedwastes. We propose a three-pronged experimental and computational approach building on our previous work in each area. We will:

- investigate kinetics in a laminar-flow reactor in which the simple flow does not confound extraction of kinetic data. *Ex situ* size-segregated particle analysis will provide data on speciation and kinetics. Drop evaporation and trajectories will be studied using *in situ* laser-induced molecular fluorescence.
- build fundamental models of drop dynamics and evaporation, reaction, particle-size evolution, gas-to-particle conversion, etc., that allow data from the laminar flow reactor at Arizona to be used to predict behavior in a larger, turbulent-flow reactor.
- use data (particle-size distribution, *ex situ* size-segregated particle analysis, etc.) From EPA's 82 kW reactor to improve and validate models that will enable rational evaluation of specific processes.

The work will contribute to rational evaluation of high-temperature thermal processes for DOE metal-bearing liquid waste through the ability to predict particle-size distribution, speciation, and size-segregated speciation. Specifically, we will address critical scientific issues relating to high-temperature reactive capture of metals from liquid wastes, including

- the chemistry of metal speciation
- the effect of drop-size variation (due to variation in feedwaste properties, such as surface tension) on thermal history of the drop, and the related effects on evaporation, kinetics, and metal speciation,
- the effect of drop size variation on drop trajectory, with special emphasis on large drops that may be-pass or penetrate the flame zone, and contribute to emissions,
- gas-to-particle conversion of metallic species, with special emphasis on the use of reactive sorbents to scavenge metallic vapors as collectable particulate, and
- the effect of operating conditions (temperature, residence time, drop size and injection velocity, turbulence intensity, and feed composition, including the metal, the liquid, and chlorine or sulfur) on the size distributions of particles formed from drops that have incompletely volatilized, as well as particles that form as a result of gas-to-particle conversion on injected sorbent.

The advantages of high-temperature reactive scavenging are:

- The organic constituents of some metal-bearing liquid wastes must be treated thermally in order to meet TSCA, RCRA, OSHA, and CAA requirements, and the laws of various states.



- No species need be added to complex liquid systems. The importance of this point is highlighted by recent DOE experience with generation of flammable amounts of benzene vapor by radiolysis of an organic complexant (sodium tetraphenylborate) used to precipitate <sup>137</sup>Cs at the Savannah River Site.
- Organics already present are destroyed with high efficiency. This is especially attractive with respect to high-level tank waste at the Hanford Site, in which large amounts of citrate, glyoxylate, EDTA, and HEDTA were added to precipitate radionuclides. These organics are important in generation of flammable gas mixtures episodically vented from 25 tanks on Hanford's Flammable Gas Watch List.
- The same basic approach can be used to treat a broad range of liquid wastes, in each case concentrating the metals (regardless of liquid-phase oxidation state or association with chelators or adsorbents) using a collectable sorbent, and destroying any organic species present.
- The general robustness with respect to gross feedwaste composition promises a relatively high degree of tolerance with respect to inevitable variations in the composition of a given metal-bearing feedwaste.

Finally, an important concern in any nuclear waste treatment process is emissions. In that regard, the Army's exemplary program to destroy stockpiled chemical weapons by incineration is instructive. Without incident, more than 1.4 million kg of nerve gas has been destroyed in two TSCA-, RCRA-, OSHA, and CAA permitted incinerators, a contract has been let for a third, and contracts for two more will be let this year. Like the Army's incineration approach for two nerve gasses and two blister agents, high-temperature reactive capture of metals from liquid waste (accompanied by incineration of any organics in the feedwaste) offers the potential for one basic process to treat (with modifications) a range of feedwastes, thus simplifying design and permitting by avoiding *de novo* process development for each waste composition.

## **Annual Progress Reports**

**1998 Progress Report**

**1999 Progress Report**

**2000 Progress Report**

**2001 Progress Report**

# Environmental Management Science Program Research in Washington

## University of Washington

### 73833 – Genetic Engineering of a Radiation-Resistant Bacterium for Biodegradation of Mixed Wastes

**Principal Investigator:** Dr. Mary E. Lidstrom

**Problem Area:** Mixed Waste

The mixture of toxic chemicals, heavy metals, halogenated solvents and radionuclides in many DOE waste materials presents a challenging problem for separating the different species and disposing of individual contaminants. One approach for dealing with mixed wastes would be to selectively remove classes of hazardous wastes from mixed waste streams producing waste streams with less complex mixtures. Enzymes exist in bacteria that detoxify halogenated organics and toxic metals such as mercury, and theoretically these could be used to selectively remove these classes of compounds from mixed wastes under mild conditions. However, bacteria containing these systems would not be expected to survive in the mixed waste streams that must be treated. Recent work with the deinococci suggests a new approach to this problem. *Deinococcus radiodurans* is a bacterium that is the most highly radiation-resistant organism known. It can survive 5 Mrad doses of gamma-irradiation, and is also highly resistant to desiccation and to peroxides. Genetic systems now exist for this organism for cloning, genetic inactivation of chromosomal genes, and expression of foreign genes, and the genome sequence has been completed. Therefore, *D. radiodurans* is a candidate for a strain that could be genetically engineered to survive in and detoxify DOE's mixed waste streams.

The goal for this project is to develop a suite of *Deinococcus radiodurans* strains for treatment of haloorganics in mixed waste streams in a optimized above-ground reactor system. The rationale for the proposed approach is based on the following required characteristics of effective treatment strains: a) high biodegradative activity; b) stable phenotype and expression characteristics in the absence of selection and in the presence of physiological stress; c) survival and activity under harsh chemical conditions.

Our proposed work will build on the progress made in the first project period for this grant, in which genetic tools have been developed for the construction of stable, high-expression strains, and used to generate first-generation treatment strains. Now we propose to extend these promising studies in the following ways: 1) development of strains with stable, regulated expression of broad spectrum oxygenases, 2) manipulation of stress response systems to generate a super-resistant detoxifier for use in the chemically extreme conditions found in mixed waste streams, and 3) development of the process parameters for using these strains to bioremediate complex waste mixtures.

By extending our current work for three more years, we will be able to produce an optimized, pilot-scale treatment system utilizing engineered strains of *D. radiodurans* to degrade haloorganics in the presence of radioisotopes, heavy metals, high ionic strength and variable pH.

## Annual Progress Report

### 2001 Progress Report

### 2002 Progress Report

# Environmental Management Science Program Research in California

## University of California at Davis

### 73843 – Mechanisms of Heavy Metal Sequestration in Soils: Plant-Microbe Interactions and Organic Matter Aging

**Principal Investigator:** Dr. Richard M. Higashi

**Problem Area:** Mixed Waste

The myriad of human activities including strategic and energy development at various DOE installations have resulted in the contamination of soils and waterways that can seriously threaten human and ecosystem health. Development of efficacious and economical remediation technologies is needed to ameliorate these immensely costly problems. Bioremediation (both plant and microbebased) has promising potential to meet this demand but still requires advances in fundamental knowledge. For bioremediation of heavy metals, the three-way interaction of plant root, microbial community, and soil organic matter (SOM) in the rhizosphere is critically important for long-term sustainability but often unconsidered. Particularly urgent is the need to understand processes that lead to metal ion stabilization in soils, which is crucial to all of the goals of bioremediation: removal, stabilization, and transformation. This renewal proposal will build on the knowledge that we have generated on the role of root exudation and metabolism for metal mobilization and accumulation, to address the following objectives:

1. Identify molecular markers and characterize the chemical nature of recalcitrant SOM pools that are involved in belowground metal ion interactions, which are likely to be markers for sustainable sequestration;
2. Utilize 1) to determine plant and microbial factors that contribute to sustainable metal sequestration or mobility, as well as bioavailability;
3. Utilize information from 1) and 2) to explore efficacious means for enhancing sustainable phytostabilization of heavymetals in the subsurface zone.

To achieve these objectives, we will conduct aging experiments using  $^{13}\text{C}$ -enriched plant matter with or without Cd, Pb, Sr, and Cs loading to trace the turnover of various organic components, and to discern chemical markers that represent recalcitrant SOM involved in interactions with heavy metal ions. The principal approach employed for this task are *in situ* organic chemical fingerprinting and turnover time measurements of whole soils by pyrolysis gas chromatography-mass spectrometry (py-GCMS) and py-GC combustion isotope ratio MS (py-GC-CIR-MS). The age markers thus obtained will be differentiated for relation to metal ion bundung by characterizing metal ion-induced chemical changes in major recalcitrant SOM (i.e. humate and humin) using py-GCMS, NMR, FT-IR, and 3-D flourescene. In turn, these metal ion-associated chemical markers will be used to follow the effect of active plant growth (involving mainly root exudation and architecture), attendant changes in microbial community, and soil aging on heavy metal stabilization, leachability, and bioavailabilty to plants. If time permits, we will also apply the approach to examine the influence of various organic residues (e.g.crop residues) on metal ion mobility and sequestration. The materials of interest are common non-polluted materials for soil cover or amendment, differing widely in organic compositions (e.g. lignin, cellulose, proteins, or pectin) which, upon diagenesis to SOM, may yield various levels of enhancement for metal sequestrian capacity.

If successful, this research should lead to fundamental advances in the understanding of plant-microbe interactions and how these interactions govern the long-term fate of heavy metals in belowground ecosystems. There should be direct applicability of these tools and knowledge to facilitate and enhance field implementation and monitoring of metal bioremediation.

**This project began in 2000. The first progress report is expected in late 2003.**

# Environmental Management Science Program Research in Maryland

## National Institute of Standards and Technology

### 73844 – Miniature Chemical Sensor Combining Molecular Recognition with Evanescent-Wave Cavity Ring-Down Spectroscopy

**Principal Investigator:** Dr. Andrew C. R. Pipino

**Problem Area:** Mixed Waste

A new chemical sensing technology is being developed that will enable remote, real-time diagnostics of chemical species in hazardous gas, liquid, and semi-solid environments with high sensitivity and selectivity. Based on a novel implementation of optical absorption, termed evanescent wave cavity ring-down spectroscopy (EW-CRDS), the technology utilizes miniature monolithic optical resonators, which are fabricated from ultra-pure optical materials. These miniature resonators employ intra-cavity total-internal-reflection (TIR) at ultra-smooth surfaces with  $\sim 0.05$  nm root-mean-square surface roughness that provide a reflectivity of  $R \cong 0.999999$ . A laser light pulse that is injected into the resonator circulates for many round trips, leading to long and accurately measurable “ring-down” times, which are highly sensitive to changes in the round-trip loss. An evanescent optical field, which is generated by TIR and decays exponentially in space outside the resonator, is absorbed by target analyte molecules at the resonator surface, resulting in a measurable change in the ring-down time. A miniscule fraction of a monolayer ( $<10^{-4}$ ) of adsorbed analyte molecules can be detected with a single laser pulse in a few microseconds.

Having achieved highly sensitive chemical detection, a key challenge remains for the EW-CRDS technology: achieving highly *selective* detection in complicated matrices. As a spectroscopic technique, some degree of selectivity is inherent to EW-CRDS, since each chemical species absorbs light at characteristic frequencies. However, in complicated matrices, absorptions may overlap when multiple absorbing species are present. Furthermore, when operating in the visible or near-infrared regions, absorption spectra are frequently broad and featureless, which further complicates the identification and quantification of absorbing species. Yet operation in the visible or near-IR regions is highly desirable to avoid absorption by water when probing aqueous media and because miniature, inexpensive diode laser sources, high transmission optical materials, and sensitive, high-speed detectors are available to facilitate the development of cost-effective, field-deployable instruments. To address the fundamental challenge of achieving high selectivity with visible or near-IR operation, we propose 1) to combine molecule recognition (MR) techniques with EW-CRDS by functionalizing the ultra-smooth TIR surfaces of the resonators to utilize selective host/guest chemical interactions, 2) to employ nanostructural resonator surfaces for which the optical and chemical properties can be tailored 3) to explore alternative forms of EW-CRDS that exploit polarization effects to increase sensitivity, selectivity, and adaptability and 4) to examine novel surface chemistry that shows inhibition of non-selective adsorption (INSA). The INSA concept may ultimately be combined with MR techniques to yield sensor surfaces that repel interferants, while having a high affinity for the analyte.

To accomplish our research plan, we have assembled a team consisting of optical scientists, synthetic chemists, and a commercial partner, along with external collaborators. The first and second year activities will focus on vapor phase sensing of trichloroethylene (TCE) and perchloroethylene (PCE). Optimum sensing conditions will be identified. Third year activities will focus on liquid phase detection, testing of INSA films, and the combination of both MR and INSA surface functionalities.

## Annual Progress Report

### 2001 Progress Report

### 2002 Progress Report

# Environmental Management Science Program Research in Kansas

## University of Kansas

### 73850– Radiation Effects on Materials in the Near-Field of Nuclear Waste Repository

**Principal Investigator:** Dr. Daryle H. Busch

**Problem Area:** Mixed Waste

With the advent of supramolecular chemistry and the growth of nanotechnology, it has become increasingly clear that molecular species and their complex aggregates can be designed and synthesized to achieve increasingly complicated and intricate goals. The present program is an example of this kind of scientific endeavor. The overall purpose of the chemistry described herein is to provide the foundations for the invention of ways in which the most powerful known kinds of ligands, or receptors, can be made useful in such applications as analytical chemistry, separations science and environmental remediation and restoration. For our purposes, a ligand is a molecular entity with the ability to fasten itself to some range of other molecular entities, forming an assembly, called a complex or coordination entity, within which the original entities remain recognizable. This program constitutes an investigation into the basic science of coordination chemistry, or supramolecular chemistry, a field that deals with all inter-molecular interactions. The subject cross-cuts all traditional chemical bordering fields: analytical, bio-, inorganic, organic, and physical chemistry, biology and materials science. The ultimate powerful ligands can capture their complements, for example, metal ions, in the most competitive of circumstances. For example ultra tight-binding ligands can remove metal ions from mineralized sites, take them away from lesser ligands, and even capture metal ions from extremely dilute solutions. In these and other related circumstances ordinary ligands, such as those used in well known separations technologies, are completely ineffective. Clearly there are compelling incentives for finding ways to apply tight-binding ligands to the management of the metallic elements under many conditions, but there are major hurdles that must be overcome to do so. A Limiting Molecular Lethargy Historically, the applications of ultra tight-binding ligands have been limited by the slow rates at which their equilibria are established. It is a fundamental fact that the equilibrium constants for the binding of any kind of receptee (e.g., a metal ion) to its complementary receptor (i.e., ligand) vary monotonically with the rates at which the receptee is liberated from the receptee/receptor complex. Consequently, ultra tight-binding ligands, whose equilibrium constants for binding exceed the ordinary binding by millions or billions of times, will release their complement at least that many millions or billions of times slower. The slowness may be even more lethargic since the rate of binding is also retarded and the equilibrium constant equals the rate of binding divided by the rate of release of the receptee from the receptor. Exploiting and Overcoming that Molecular Lethargy In order to make best use of tight-binding receptors it is, therefore, necessary to either accommodate any specific methodology to these slow kinetic processes or to find means of accelerating the formation and dissociation rates associated with complexation. This proposal aims at both targets and the attainment of these goals will produce a legacy of new principles and general methodologies that will provide the foundations for many important applications. This document is organized in terms of those goals. In each case we are specifically concerned with the proof of concept, generalization of the concept, and definition of general methodologies. The three concept areas are: (1) Switch binding of templating ligands—accelerate the rate of binding by templating the final step in synthesis of a tight-binding ligand upon contact with the target metal ion. (2) Switch release of photo reactive ligands—accelerate the rate of release of a metal ion from a tight-binding ligand by incorporating photorelease, and possibly other environmentally clean release features, into the ligand structures. (3) A slow technology based on imprinted polymers (e.g., a soil poultice)—design a separations methodology based on the dual selectivity of ligand/metal ion interaction combined with host/guest interaction between the metal-ligand complex and an imprinted polymer. This soil poultice is well adapted to slow kinetics of reaction between unmodified tight-binding receptor/receptee pairs.

## **Annual Progress Report**

### **2001 Progress Report**



## Environmental Management Science Program Research in California

### Rockwell International Corporation

#### 55094 – Chemical and Ceramic Methods Toward Safe Storage of Actinides Using Monazite

**Principal Investigator:** Dr. P. E. D. Morgan

**Problem Area:** Nuclear Materials

The program will address more particularly the section, "Plutonium behavior in mixed matrices - specialized waste forms", with the concept that monazite ceramic will provide the most safe, most secure, geologically tested, very long term, containment for actinides. That monazites are the ideal crystal hosts for containment of actinide or transuranic elements (extremely stable geologically and resistant to radiation damage) is well established. They were proposed a number of years ago as high level nuclear waste forms at Oak Ridge National Laboratory.

Following the deliberations of the Hensch Panel in 1984, and the decision to proceed with borosilicate glass as a low level waste, organized research on monazite and other "alternative waste forms" came to an end. As pointed out in a current National Academy of Science Panel report, approximately fifteen years of potential progress in the development of alternative nuclear waste forms were then lost.

We therefore seek to do basic studies of the ceramic nature of monazite utilizing two groups that have a serious previous background in research concerning monazite and radwaste encapsulation. These are complicated fields and, to avoid unnecessary duplication and waste, it should be important to utilize and to extend that already hard won experience.

The group headed by Lynn Boatner at Oak Ridge National Labs has many years of preeminent experience in studying monazite, while that laboratory is, naturally, in a fine position to transfer basic study results to later engineering application.

The group at the Rockwell Science Center, including Alan Harker and Peter Morgan, became well known for its work in the area of ceramic radwaste hosts and contributed considerable basic understanding to the ceramic problems and advantages, particularly pointing out to the community the key role of the grain boundary leaching phenomena (possible glasses, precipitated grain boundary phases, etc.).

The recent discovery by the Rockwell group, including also David Marshall, that monazite provides weak stable interfaces for ceramic matrix composites has stimulated widespread, renewed interest in the properties of monazite as a ceramic.

The main outstanding fundamental research issues facing the use of monazite as a waste form necessitate the development of fundamental understanding of: sintering mechanisms involved in forming high density monazite ceramics; physical and chemical properties of grain boundaries in these ceramics; interactions with impurities and additives used to promote densification; physical properties of polycrystalline monazite

ceramics; and the precipitation of monazite phases in an efficient, simple and economical manner. We propose to address these issues to serve as a knowledge base for using monazite as a nuclear waste form.

## **Annual Progress Reports**

**1997 Progress Report**

**1998 Progress Report**



# **Environmental Management Science Program Research in Illinois**

## **University of Illinois at Chicago**

### **60247 – Miniature Nuclear Magnetic Resonance Spectrometer for In-Situ and In-Process Analysis and Monitoring**

**Principal Investigator:** Dr. Gennady Friedman

**Problem Area:** Nuclear Materials

The objective of this research project is to develop a new analytical instrument based on the principle of nuclear magnetic resonance (NMR) for in-situ, in-field and in-process characterization and monitoring of various substances and chemical processes. The new instrument will be a highly miniaturized version of an NMR spectrometer and its development will involve application of the most recent advances in the fields of micromachining and microfabrication, permanent magnet materials and design, and microelectronics and signal processing. The proposed miniature NMR spectrometer will be a hand-held unit weighing around 5-6 pounds and intended to perform measurements on liquid samples of micro- to nano-liter volumes. The resolution of the instrument is projected to be better than 0.1 ppm (part per million) with sensitivities approaching 10 to 100 ppm (1 millimolar to 10 millimolar) for proton containing molecules. While initial developments will focus on applications of proton NMR, further developments will be aimed at other nuclei, such as  $^{19}\text{F}$ ,  $^{31}\text{P}$  and  $^{13}\text{C}$ . Applications of the miniature NMR system will include down hole monitoring of ground water pollutants and flow, real-time in-process monitoring of waste remediation activities, spatial composition analysis in chemical and waste storage tanks, in-field characterization of waste materials and many others.

## **Annual Progress Report**

### **1999 Progress Report**

# **Environmental Management Science Program Research in California**

## **Lawrence Livermore National Laboratory**

### **60319 – Thermodynamics of the Volatilization of Actinide Metals in the High-Temperature Treatment of Radioactive Wastes**

**Principal Investigator:** Dr. Tom Wolery

**Problem Area:** Nuclear Materials

We are proposing to perform a detailed study of the volatilization behavior of the U, Pu and possibly Am under conditions relevant to the thermal treatment (destruction) of actinide-containing organic-based mixed and radioactive wastes. The primary objective of this 3-year project is to develop a basic scientific (thermodynamic) understanding of actinide volatilization and partitioning/speciation behavior in the thermal processes that are central to DOE/EM's mixed waste treatment program. The work is a combination of experimental studies and thermodynamic modeling. Transpiration and mass spectrometric measurements will be made to determine U, Pu and possibly Am volatile species and the extent of their volatilization when  $\text{UO}_2/\text{U}_3\text{O}_8$ ,  $\text{PuO}_2$  and  $\text{AmO}_2$  are heated to temperatures of 500 to 1600°C under (i) pyrolyzing (reducing) conditions, and (ii) oxidizing conditions (i.e.  $\text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$  mixtures) in the presence of chlorine ( $\text{Cl}_2(\text{g})$  or  $\text{HCl}(\text{g})$ ). Work on uranium volatilization under reducing conditions will be performed in a laboratory at U.C. Berkeley in a collaboration with Professor D.R. Olander. In parallel with the experimental effort, a complete thermodynamic database for expected actinide gaseous species will be developed from literature data, from the proposed measurements, and from data predictions using bond energy correlation and statistical thermodynamics estimation methods.

## **Annual Progress Report**

### **1999 Progress Report**



## Environment Management Science Program Research in Michigan

### The University of Michigan

#### 59849 – Radionuclide Immobilization in the Phases Formed by Corrosion of Spent Nuclear Fuel: The Long-Term Assessment

**Principal Investigator:** Dr. Rodney C. Ewing

**Problem Area:** Spent Nuclear Fuel

The  $\text{UO}_2$  in spent nuclear fuel is not stable under oxidizing conditions. Under oxic conditions, the U(IV) has a strong tendency to exist as U(VI) in the uranyl molecule,  $\text{UO}_2^{2+}$ . The uranyl ions react with a wide variety of inorganic and organic anions to form complexes which are often highly soluble. The result is rather rapid dissolution of  $\text{UO}_2$  and the formation of a wide variety of uranyl oxide hydrates, uranyl silicates and uranyl phosphates. The reaction rates for this transformation are rapid, essentially instantaneous on geologic time scales. Over the long term, and depending on the extent to which these phases can incorporate fission products and actinides, these alteration phases become the near-field source term.

Fortunately, previous investigations (experimental studies and field studies) have established that natural uraninites and their alteration products can be used as *natural analogues* to study the corrosion of  $\text{UO}_2$  in spent nuclear fuel. We propose in this research program to address the following issues:

1. What are the long-term corrosion products of natural  $\text{UO}_2+x$ , uraninite, under oxidizing conditions?
2. What is the paragenesis or the reaction path of the phases that form during alteration? How is the paragenetic sequence formation related to the structures and compositions of these uranyl phases?
3. What is the trace element content (as compared to the original  $\text{UO}_2+x$ ), and does the trace element content substantiate models developed to predict fission product and actinide incorporation into these phases?
4. Are these the phases that are predicted from reaction path models (e.g., EQ3/6) which will be used in performance assessments?
5. How persistent over time are the metastable phase assemblages that form? Will these phases serve as barriers to radionuclide release?
6. Based on the structures of these phases (mostly sheet structures) can the thermodynamic stabilities of these phases be estimated, or at least bounded, in such a way as to provide for a convincing and substantive performance assessment?

This research is based on over a decade of previous work on uranium mineralogy, paragenesis, and the corrosion of  $\text{UO}_2$  by the principal investigator, R. C. Ewing.

## **Annual Progress Reports**

**1998 Progress Report**

**1999 Progress Report**

**2000 Progress Report**

## **Environmental Management Science Program Research in Indiana**

### **University of Notre Dame**

#### **59960 – Direct Investigations of the Immobilization of Radionuclides in the Alteration Products of Spent Nuclear Fuel**

**Principal Investigator:** Dr. Peter C. Burns

**Problem Area:** Spent Nuclear Fuel

As part of the stated proposal, work at Argonne National Laboratory (ANL) will emphasize the synthesis of uranium phases and uranium phases doped with certain radionuclides in order to examine radionuclide incorporation in uranyl compounds. The identities of alteration phases important for spent-fuel corrosion will be gleaned from the results of long-term experiments on the corrosion of spent  $\text{UO}_2$  fuel and unirradiated  $\text{UO}_2$ , as well as more recent studies of U-metal fuel corrosion, that are currently underway at ANL. We will focus on synthesizing actinide compounds similar to those that have been identified as corrosion products of spent uranium-based fuels. The goals of the experiments are to synthesize and characterize actinide and fission-product host phases formed on U-based waste forms under oxidizing conditions, such as expected at the candidate geological repository at Yucca Mountain. Target phases for synthesis include those identified in current corrosion experiments with U-based fuels being conducted at Argonne. Those experiments demonstrate that many radionuclides are retained in U-bearing alteration products. Synthesis and characterization of U(VI) phases doped with specific radionuclides helps clarify the mechanisms of radionuclide incorporation into uranyl-based compounds. Where possible, stable-isotope equivalents of radionuclides are used during synthesis; however, pure Np and Pu analogues of selected uranium compounds will also be synthesized. In addition, U compounds doped with low levels of selected radionuclides will be characterized in order to understand mechanisms of trace-element substitution. Methods used to characterize solid phases include X-ray powder diffraction and transmission electron microscopy. Selected samples are also analyzed by single-crystal X-ray structure analyses and X-ray absorption spectroscopy, where possible.

### **Annual Progress Reports**

**1998 Progress Report**

**1999 Progress Report**

**2000 Progress Report**

## **Environmental Management Science Program Research in the District of Columbia**

### **Naval Research Laboratory**

#### **60141 – Gamma Ray Imaging for Environmental Remediation**

**Principal Investigator:** Dr. W. Neil Johnson

**Problem Area:** Spent Nuclear Fuel

The research is a three year development program to apply high resolution gamma-ray imaging technologies to environmental remediation of radioactive hazards. High resolution, position-sensitive germanium detectors are being developed at the Naval Research Laboratory for space applications with support from the Office of Naval Research and the National Aeronautics and Space Administration. In the program, we will model the performance of these detectors for direct imaging of spent nuclear fuels and fissile materials and Compton scatter imaging of large objects of arbitrary size, investigate fabrication of field-usable detectors, and demonstrate the performance of such a system using a small configuration of detectors.

### **Annual Progress Reports**

**1998 Progress Report**

**1999 Progress Report**

**2000 Progress Report**

## **Environmental Management Science Program Research in Indiana**

### **University of Notre Dame**

#### **73691 – Renewal of Direct Investigations of the Immobilization of Radionuclides in the Alteration Products of Spent Nuclear Fuel**

**Principal Investigator:** Dr. Peter C. Burns

**Problem Area:** Spent Nuclear Fuel

As part of the stated proposal, work at Argonne National Laboratory (ANL) will emphasize the synthesis of uranium phases and uranium phases doped with certain radionuclides in order to examine radionuclide incorporation in uranyl compounds. The identities of alteration phases important for spent-fuel corrosion will be gleaned from the results of long-term experiments on the corrosion of spent  $\text{UO}_2$  fuel and unirradiated  $\text{UO}_2$ , as well as more recent studies of U-metal fuel corrosion, that are currently underway at ANL. We will focus on synthesizing actinide compounds similar to those that have been identified as corrosion products of spent uranium-based fuels. The goals of the experiments are to synthesize and characterize actinide and fission-product host phases formed on U-based waste forms under oxidizing conditions, such as expected at the candidate geological repository at Yucca Mountain. Target phases for synthesis include those identified in current corrosion experiments with U-based fuels being conducted at Argonne. Those experiments demonstrate that many radionuclides are retained in U-bearing alteration products. Synthesis and characterization of U(VI) phases doped with specific radionuclides helps clarify the mechanisms of radionuclide incorporation into uranyl-based compounds. Where possible, stable-isotope equivalents of radionuclides are used during synthesis; however, pure Np and Pu analogues of selected uranium compounds will also be synthesized. In addition, U compounds doped with low levels of selected radionuclides will be characterized in order to understand mechanisms of trace-element substitution. Methods used to characterize solid phases include X-ray powder diffraction and transmission electron microscopy. Selected samples are also analyzed by single-crystal X-ray structure analyses and X-ray absorption spectroscopy, where possible.

### **Annual Progress Report**

#### **2001 Progress Report**

# Environment Management Science Program Research in Michigan

## The University of Michigan

### 73751 – Corrosion of Spent Nuclear Fuel: The Long Term Assessment

**Principal Investigator:** Dr. Rodney C. Ewing

**Problem Area:** Spent Nuclear Fuel

Spent nuclear fuel accounts for over 95% of the total radioactivity in the radioactive wastes in the United States that require disposal, disposition or remediation. Uranium is the dominant actinide element in most of these nuclear wastes. The  $\text{UO}_2$  in spent nuclear fuel is not stable under oxidizing conditions and may be altered even under reducing conditions.

Under oxidizing conditions, uranium has a strong tendency to exist as  $\text{U}^{6+}$  in the uranyl molecule,  $\text{UO}_2^{2+}$ . The uranyl ion reacts with a wide variety of inorganic and organic anions to form complexes that are often highly soluble. The result is a rather rapid dissolution of  $\text{UO}_2$  and the formation of a wide variety of uranyl oxide hydrates, uranyl silicates and uranyl phosphates. The kinetics for this transformation is rapid and essentially instantaneous on geologic time scales.

Under reducing conditions,  $\text{UO}_2$  is stable, but may alter to  $\text{U}^{4+}$  compounds, such as coffinite,  $\text{USiO}_4$ , depending on ground water compositions.

Under both oxidizing and reducing conditions, the formation of new uranium phases may lead to the release or retardation of trace elements, such as the fission product elements and actinides in spent nuclear fuel. Over the long term, and depending on the extent to which the secondary uranium phases can incorporate fission products and actinides, *these alteration phases become the near-field source term*.

Fortunately, our experimental analysis and field studies have established that natural uranite and its alteration products are good “natural analogues” for the study of the corrosion of  $\text{UO}_2$  in spent nuclear fuel. We propose in this research program to address the following issues:

1. What are the *long-term* corrosion products of natural  $\text{UO}_{2+x}$ , uranite, under oxidizing and reducing conditions?
2. What is the paragenesis or the reaction path for the phases that form during alteration? How is the sequence of formation related to the structure of these uranium phases and reacting ground water composition?
3. What is the trace element content in the corrosion products as compared with the original  $\text{UO}_{2+x}$ ? Do the trace element contents substantiate models developed to predict radionuclide incorporation into the secondary phases?
4. Are the corrosion products accurately predicted from geochemical codes (e.g., EQ3/6) that are used in performance assessments?
5. How persistent over time are the metastable phase assemblages that form? Will these phases serve as effective barriers to radionuclide release?
6. Experimental results and theoretical models for the corrosion of spent nuclear fuel under oxidizing and reducing conditions will be tested by comparison to results from studies of samples from the Oklo natural fission reactors.

## Annual Progress Report

### 2001 Progress Report

### 2002 Progress Report



## **Environmental Management Science Program Research in the District of Columbia**

### **Naval Research Laboratory**

#### **73839 – Gamma Ray Imaging for Environmental Remediation (GRIER)**

**Principal Investigator:** Dr. W. Neil Johnson

**Problem Area:** Spent Nuclear Fuel

We propose a three-year continuation of our program to apply high-resolution gamma-ray imaging technologies to environmental remediation of radioactive hazards. High resolution, position-sensitive germanium detectors offer excellent capabilities for the detection, identification and characterization of radioactive isotopes. These detectors provide enhanced capabilities over existing systems and have direct applicability in the areas of Decontamination and Decommissioning (D&D), Nuclear Materials, Spent Nuclear Fuel (SNF), Mixed Waste, as well as for basic nuclear physics. In the first two years of our current research program, we have successfully demonstrated all aspects of the proposed program- amorphous Ge contact fabrication and the development of a 2x2 array of detectors for field demonstrations. The objective of the continuation program is the combination of these two successes into an array of ~6x larger detectors with amorphous Ge contacts. By the end of the three-year continuation program, we plan to demonstrate a prototype that can be commercialized and used in the field.

**This project began in 2001. The first progress report is expected in late 2003.**



## Environmental Management Science Program Research in Massachusetts

### Woods Hole Oceanographic Institution

#### 54683 – Speciation and Structural Characterization of Plutonium and Actinide-Organic Complexes in Surface and Groundwaters

**Principal Investigator:** Dr. Ken O. Buesseler

**Problem Area:** Subsurface Contamination

We are studying the chemical nature of the actinides and their association with specific organic ligands in the natural environment. We will bring to this study a range of newly developed technologies which the PI's have used to study the physical organic and structural features of dissolved organic matter (DOM) and the association of trace metals and radionuclides with the particulate, colloidal and dissolved phases. The application of cross-flow ultrafiltration (CFU) techniques will allow us to quantitatively recover DOM from surface and groundwater, and separate it without significant loss into different size classes, ranging from 1 kilo-Dalton (kD) to 100 kD (e.g. Buffle *et al.*, 1992). Given such samples, we can thus assess for each fraction the total colloidal actinide binding activity, but more importantly, we will isolate, purify, and structurally characterize actinide-binding polymers in natural waters. The application of thermal ionization mass spectrometry (TIMS) is essential for the detection of Pu, Np and U for this study. Most importantly, TIMS will provide: a) the sensitivity needed to make these measurements on small samples at ambient fallout levels and in the far field migration of groundwater actinides; b) the ability to use isotope ratios to distinguish between fallout and other possible sources; and c) will allow us to compare the *in-situ* behavior of a suite of actinides with similar sources but differing environmental geochemistries (Buesseler and Halverson, 1987; Stoffel *et al.*, 1994).

Conceptual and analytical advances made over the last decade have significantly altered our view of DOM in aquatic systems and the approach taken to study actinide-organic complexation. The traditional view that actinide-organic matter complexation is primarily with humic substances may be incorrect. Non-humic DOM may support much of the actinide binding activity of colloids. DOM may not be a poorly structured assembly of random polymers, but may include a large fraction of highly ordered biopolymers. The sites to be chosen for study therefore span a range of DOM characteristics and redox settings. Given the labor intensity of the analyses we would focus on a limited range of sites, but a wide range of geochemistries. We would optimize our sampling and analytical strategies during the first year using samples from organic-rich fresh water ponds in the Woods Hole area. Subsequent field trips (one in each of years 2 and 3) would be conducted to sites where there is contrasting geochemistry's for study and some concern about migration of actinides from waste sources. One proposed site is at the Savannah River Facility, where a previous study of monitoring wells adjacent to an unlined seepage basin, suggests that Pu(IV) organic colloids have migrated much more rapidly than predicted ( $> 1$  km- Kaplan *et al.*, 1994). Finally, we will also sample subsurface waters from the Hanford Reservation with assistance from our colleagues from Pacific Northwest Lab (PNL). This will allow for a comparison of actinide speciation between surface and subsurface waters and permit us to examine the relative transport of Pu originating from global fallout and waste related sources (separated via TIMS isotopic analyses).

Once collected, samples would be split. Total radionuclide, organic and supporting geochemical measurements, and CFU processing would be conducted in the field for isolation of the colloidal size-classes. For the radionuclides, we would measure not only total concentration using TIMS analyses, but also perform redox separations to determine for example, the relative abundance of the more oxidized or reduced forms of Pu in the colloidal vs. ultrafiltrate size-classes. Of particular interest is how the redox chemistry of Pu varies as a function of ambient DOM levels and site specific characteristics. The structural characteristics of the DOM will be determined using a range of techniques, including 2-D NMR, high resolution electrospray MS/MS, and pyrolysis-GC/isotope ratio MS. An important feature of this approach is that we can then integrate information on molecular composition (simple sugars, amino acids and lipids, etc.) with information on polymer structure (Aluwihare *et al.*, 1996). The importance of understanding the macromolecular features of DOM cannot be over emphasized. Previous models which have treated colloidal organic matter as a single phase or have limited chemical characterization to humic substances only, have not been successful in describing metal binding activity and physical chemical characteristics of DOM.

## **Annual Progress Reports**

**1997 Progress Report**

**1998 Progress Report**

**1999 Progress Report**

**2000 Progress Report**

# Environmental Management Science Program Research in California

## Stanford University

### 54699 – The Use of Dielectric and NMR Measurements to Determine the Pore-Scale Location of Organic Contaminants

**Principal Investigator:** Dr. Rosemary Knight

**Problem Area:** Subsurface Contamination

A critical step in achieving the cost-effective treatment of a contaminated region of the subsurface is the initial design stage. The design of an effective treatment scheme for a contaminated site requires knowledge of the *in situ* physical and chemical state of the contaminant. A first-order problem in characterizing the *in situ* state of non-aqueous phase contaminants is determining the pore-scale distribution and mobility of the contaminant. Of specific interest in this research is determining the wettability of the system; i.e. is the contaminant present as an immiscible *non-wetting* phase located in the central volume of the pore space, or does the contaminant exist as a *wetting* phase that is adsorbed to, or coating, the solid surface. We plan to investigate, through an extensive laboratory study, the concept that measurements of the dielectric constant and nuclear magnetic resonance (NMR) can be used to determine wettability and thus discriminate between these two cases.

Wettability is defined as the tendency of one fluid to adsorb to, or to coat, a solid surface in the presence of other immiscible fluids (Craig, 1971). Water strongly wets most rock-forming minerals, but some oils, for example, can "out-compete" the water for the solid surface causing the "water-wet" rock to become "oil-wet". The wettability is a critical factor in determining the pore-scale location of the immiscible fluids and the movement of the fluid phases. While studies of wettability have long been an important part of understanding and modeling multi-phase flow in hydrocarbon reservoirs, there has been relatively little attention paid to the role of wettability in contaminant transport and remediation, even when the contaminant is an oil. In fact, it is generally assumed in an oil-water-air system that water is the wetting phase. As reviewed in a recent paper (Bradford and Leiji, 1996) this is not true for many natural systems, and the assumption of a water-wet state can lead to grossly inaccurate predictions of capillary pressure-saturation relationships, and the mobility of the contaminant. Determining wettability is thus a critical factor in site characterization.

Our past research has clearly shown a link between the dielectric and NMR response of geological materials and the wettability of the material. This has introduced the intriguing possibility that the combined use of dielectric and NMR measurements can be used as a means of characterizing the wettability of a geological system. For field applications, ground penetrating radar (GPR) is a high frequency electromagnetic technique that can be used to measure the dielectric properties of the subsurface in the frequency range of 10 MHz to 1 GHz. The current development of a geophysical technique referred to as very early time electromagnetics (VETEM) will provide a means of obtaining measurements of dielectric properties at lower frequencies, in the range of 10 kHz to 150 MHz (Pellerin et al., 1995). Measurement of the *in situ* NMR response of materials in the subsurface can be made with NMR borehole systems, and by using a surface measurement system, recently developed and now commercially available. The interest in this research is the potential use of both GPR and/or VETEM, and NMR as a means of characterizing the *in situ* physical and chemical state of an organic contaminant in the subsurface.

The objectives of the research do not involve any analysis of the field methods. The use of the field techniques provides information about the dielectric constant and the NMR relaxation time of the subsurface. Our focus is exclusively a laboratory study aimed at developing a fundamental understanding of the link these two parameters and the pore-scale location of a contamination. Specifically - can we discriminate, with dielectric and NMR measurements, between a water-wet system in which water coats the solid surface, and a system in which an organic contaminant is absorbed to the solid?

We will first prepare a suite of unconsolidated samples with varying wettability; then measure both the dielectric and NMR response of the samples as a function of solution chemistry. Both the composition of the wetting film and solution chemistry can affect wettability and will be the two key parameters in this study. The results of this comprehensive laboratory study will provide us with the data set necessary to both model and predict the dependence of dielectric properties and NMR on wettability. This will contribute significantly to a long-term research objective which is to assess the combined use of GPR and/or VETEM, and NMR to discriminate, *in situ*, between the wetting versus non-wetting behavior of contaminants.

## **Annual Progress Reports**

**1997 Progress Report**

**1998 Progress Report**

**2000 Progress Report**

# Environmental Management Science Program Research in California

## Stanford University

### 54860 – Sorption of Heavy Metals and Radionuclides on Mineral Surfaces in the Presence of Organic Co-Contaminants

**Principal Investigator:** Dr. James O. Leckie

**Problem Area:** Subsurface Contamination

A review of the known inventory of chemical wastes at DOE facilities reveals that a large fraction of the waste is present as complex mixtures containing radionuclides, heavy metals, fuels, oils, organic solvents, and a variety of organic metal complexing agents (Riley and Zachara 1992). This situation is a result of a history of co-disposing wastes associated with chemical processing, metal surface cleaning, decontamination, and fabrication procedures used in the production of nuclear fuels and weapon components. Similar conditions also exist in industry where mixed wastes with heavy metals and chelating agents have been produced. The large inventory of complex and potentially unstable wastes must be stored until suitable treatment, confinement or disposal technologies have been developed. Unfortunately, in many cases the waste materials have been either discharged directly into open pits, or have since escaped from temporary containment facilities and now contaminate surrounding soils and groundwater.

The chemical complexity of these wastes present particularly challenging problems with respect to predicting subsurface migration of the radionuclides and heavy metals, and developing suitable remediation strategies. Among the organic compounds at DOE sites are a number of organic chelating agents that can form stable solution complexes with metals, radionuclides, and their oxy-ions. Examples include EDTA<sup>1</sup>, NTA<sup>2</sup>, and citric acid. It would be reasonable to predict that the formation of metal-organic complexes, especially those with stable multi-dentate structures, will influence the mobility of the metals and radionuclides in soils and groundwater. A general prediction that is consistent with the few available field studies would be that metal complexing organic ligands should increase metal mobility. This has already been demonstrated in a number of studies (e.g., Means et al., 1978; Girvin et al., 1993; Zachara et al., 1995). However, recent work with uranium and citric acid (Redden et al., 1996) and cadmium and citric acid (Boily and Fein, 1996) on metal oxides has shown that, under particular chemical conditions, complexing agents can actually enhance metal adsorption. Mobility of ionic solutes in groundwater is a function of the extent of partitioning between the mobile (water) and immobile (soil, mineral) phases. Organic ligands compete with reactive surface binding sites for metal solutes, or bind directly to surfaces thereby altering the type and availability of binding sites. In most field applications, increased mobility of soil and groundwater contaminants is not desirable since retrieval of the contaminants or isolating the public from hazardous conditions becomes more difficult as zones of contamination expand. However, in some cases, where remediation involves contaminant recovery, maximum mobility can be a distinct advantage.

At present, with the available experimental database, broad generalizations concerning the effect of organic ligand and chelating agents on metal or radionuclide mobility cannot be made. The quantitative predictions of partitioning that are necessary to estimate contaminant transport are not yet possible, and specific details of the chemical mechanisms are still hypothetical. In order to make reasonable transport predictions, an expanded database is needed for a range of priority heavy metal contaminants, common ligands, and representative mineral surfaces. Elucidating the mechanisms by which organic ligands affect metal partitioning at surfaces will provide information necessary for the design of effective treatment strategies.

<sup>1</sup> Ethylenediaminetetraacetic acid

<sup>2</sup> Nitrilotriacetic acid

## **Annual Progress Reports**

**1997 Progress Report**

**1998 Progress Report**

# **Environmental Management Science Program Research in Washington**

## **University of Washington**

### **54889 – Using Trees to Remediate Groundwaters Contaminated with Chlorinated Hydrocarbons**

**Principal Investigator:** Dr. Stuart E. Strand

**Problem Area:** Subsurface Contamination

Phytoremediation has emerged as a treatment alternative that combines the low cost of intrinsic remediation with the more active and adaptable characteristics of conventional remediation. Our lab has shown that fast-growing and deep-rooted hybrid poplar take up and transpire trichloroethylene (TCE) at a high rate, and that significant amounts of TCE are oxidized to carbon dioxide. These findings have been confirmed with axenic tissue cultures and with unique laboratory bioreactors that provide complete mass balance accounting of the fate of TCE carbon with whole plants. Ongoing field trials of small plots of poplar exposed to TCE have provided striking confirmation of the ability of these trees to completely prevent the movement of TCE through a barrier of densely planted poplar. We have also made significant progress in identifying the mechanism of TCE degradation in poplar (cytochrome P-450 IIE 1) and in constructing transgenic plants with enhanced capability for degradation of chlorinated hydrocarbons (CHCs). Finally recent evidence suggests that poplar will also be capable of uptake and oxidation of carbon tetrachloride.

We propose to test the ability of several plant clones to take up and transform various CHCs, including carbon tetrachloride, chloroform, dichloromethane, 1,1,1-trichloroethane, perchloroethylene, trichloroethylene, the dichloroethylenes, and vinyl chloride using laboratory mass balance reactors. Screening methods have been developed that permit testing of plants from contaminated sites for those able to oxidize and sequester chlorinated compounds. In order to predict the best location and size of the plantation and hydrogeological models will be developed which include uptake of water and pollutants from the aquifer by trees. We will identify the mechanisms involved in CHC oxidation in poplar. We enhance that activity by amplifying expression of native monooxygenases or mammalian P-450s in poplar.

We anticipate that these approaches will provide powerful new tools for the remediation arsenal: selfmaintaining, solar-driven, pump-and-treat systems.

### **Background and Significance**

Industrial practices in the past have resulted in contamination of groundwater with chlorinated hydrocarbons (CHCs) at many DOE sites, such as Hanford and Savannah River. Such contamination is a major problem because existing groundwater remediation technologies are expensive and difficult. An inexpensive method for groundwater remediation is greatly needed.

An alternative to costly conventional technologies is intrinsic remediation, which uses natural processes intrinsic to some polluted groundwaters that result in degradation, dilution or immobilization of the pollutant before adverse health effects can occur. Unfortunately not all sites have the requisite conditions to permit intrinsic remediation to occur at a rate which make it a viable option. Frequently, it is unclear whether there is sufficient electron donor present to maintain the requisite anaerobic conditions to sustain intrinsic remediation of CHCs for the time required to treat all of the pollutant that may be present. Furthermore, intrinsic remediation relies on natural groundwater flow to flush the polluted aquifer clean, extending the time required for cleanup.

Recently another option has emerged that combines the minimal intervention and costs of intrinsic remediation with the more active and adaptable characteristics of conventional remediation approaches. This option is phytoremediation and the University of Washington has taken a leading role in its



application to groundwaters polluted with CHCs. Phytoremediation is the use of plants to clean up contaminated soil, water and air.

Trees could be used to provide an active remediation zone and barrier to pollutant movement at minimal cost. Cost analysis suggests that phytoremediation would cost less than half the cost of conventional pump-and-strip technology over the 30-year life of the project. Since most of the cost of phytoremediation would be due to monitoring requirements, this outlay would be comparable to that required for intrinsic remediation. Poplar wood is valuable as a source of chips for paper making and its sale would partially offset the cost of phytoremediation. Poplar grow rapidly, reaching 30 m in nine years. Their roots seek out water from depths up to 20 m. Their transpiration rate is very high and their ability to prevent the movement of nitrate contaminated water off agricultural sites has been well demonstrated. Approximately 80% of the CHC polluted aquifers in the US are within 20 m of the surface, thus potentially accessible to poplar roots.

Poplar could be used to assist in the clean up of the contaminated groundwater at Hanford with beneficial effects on the major mobile pollutants: nitrate, carbon tetrachloride and tritium. A phytoremediation barrier could be established across the contaminated plume as it approaches the Columbia River. Near the river the plume is shallow enough for trees to access the groundwater. A sufficiently large plantation of densely planted poplar could prevent the plume from reaching the river. These trees would easily take up and assimilate the nitrate. Tritium contaminated water would be assimilated into plant tissue and transpired to the atmosphere, where sufficient dilution exists to prevent serious harm. Carbon tetrachloride would be transpired, metabolized and sequestered in plant tissue, and oxidized to carbon dioxide, depending on the trees planted. Over the lifetime of the plantation (50 years or more) trees would be harvested, sold for pulp, and new trees would be planted. A poplar plantation barrier would be much less expensive than other active remediation technologies.

Before phytoremediation can be extensively applied, we must determine the range of compounds that are attacked, the effects of metabolic products on the plants and the environment, and the effect of transpiration and concentration of CHC on uptake and metabolism. Aside from TCE very little is known of what other CHCs can be transported and/or oxidized by plants. A survey should be made of the CHC degradation ability of trees adapted to growth in various locales so that phytoremediation can be applied across the country. Little is known about the distribution of CHC degradation capability in plants. These capabilities should be surveyed by testing a wide variety of plants. Trees already growing on contaminated sites should be tested to determine if they have adapted by metabolizing the pollutants. Hydrogeological models that include the effects of trees on groundwaters polluted with CHCs are needed to provide rules for designing phytoremediation plantations. In order to capitalize on the promise of phytoremediation as illustrated by our findings of TCE metabolites in poplar tissue, we need to understand the mechanisms of plant metabolism of TCE and to explore transgenic mechanisms for increasing TCE degradation.

## **Annual Progress Reports**

### **1997 Progress Report**

### **1998 Progress Report**

### **2000 Progress Report**

## **Environmental Management Science Program Research in New Mexico**

### **New Mexico Institute of Mining & Technology**

#### **55109 – New Permeameters for In Situ Characterization of Unsaturated Heterogeneous Permeability**

**Principal Investigator:** Dr. John L. Wilson

**Problem Area:** Subsurface Contamination

Thick unsaturated zones underlie many DOE landfills, industrial areas, and waste storage sites in the western United States (U.S.) and are the primary pathway for contaminants to migrate into underlying aquifers. The spatial variability of unsaturated permeability in these heterogeneous geologic materials directly influences the movement of water and non-aqueous phase liquids (NAPL's), precluding meaningful modeling of contaminant transport for risk assessment or remediation design. In unsaturated materials, the influence of heterogeneity on flow and transport processes is amplified by capillary forces, because permeability is a function of both geologic heterogeneity and the fluid saturation. Poor characterization of heterogeneity may lead to ineffective remedial designs and increased risk, requiring subsequent additional remedial actions at increased cost and time. There are techniques that incorporate site-specific heterogeneity into a probabilistic risk framework for decision analysis, but they cannot be applied to the unsaturated zone with confidence. It is presently not possible to collect the large number of data they need to accurately define the spatial correlation structure of unsaturated permeability. Laboratory methods for estimating the unsaturated permeability are expensive, time-consuming, and may not yield results representative of heterogeneous field conditions. This project is aimed at the design, development and testing of new rapid, and cost effective field methods for estimating *in situ* unsaturated permeability.

### **Annual Progress Reports**

**1997 Progress Report**

**1998 Progress Report**

**1999 Progress Report**

# Environmental Management Science Program Research in California

## University of California at Davis

### 55118 – Plant Rhizosphere Effects on Metal Mobilization and Transport

**Principal Investigator:** Dr. Teresa W-M. Fan

**Problem Area:** Subsurface Contamination

Among the factors that influence metal availability to soil-grown plants, one of the least understood is the influence of root/soil interfaces on metal mobilization and subsequent transport into the root. These include root exudation for chelating and reducing metal ions, cell wall binding of metal ions, and root-microbial associations. Past research efforts, aimed largely at understanding plant iron deficiency, have focused on specific chelating agents that are released by plant roots and microorganisms to facilitate iron solubilization and uptake (Crowley and Gries, 1994; Manthey et al., 1994). Although there have been some hints that root exudation may also govern mobilization and transport of other trace metals, a mechanistic understanding of the process for mobilization of metals other than iron is lacking. Any progress in this area will first require identifying root exudate and cell wall components which may serve as metal chelating or reducing agents. It is also necessary to examine microbial metabolites, such as siderophores that are released into the rhizosphere, and the alteration of root exudates by root associated microorganisms. In this research, we propose a comprehensive profiling of root exudate and cell wall components that will greatly facilitate the identification of metal mobilizing compounds, and will study the composition of metal mobilizing substances in the rhizosphere as affected by mycorrhizae and other soil microorganisms.

The first objective of the research will be to determine the biochemical composition of root exudates, with a particular focus on metal-binding organic acids, and changes in their composition and biosynthesis in response to selected metals. Since grasses are considered to have many desirable characteristics for use in bioremediation, and produce phytosiderophores that are known to mobilize various metals, we will use wheat (*Triticum aestivum*) as a model plant species. For our initial experiments, we will characterize the effects of selected metals on root exudates released by plants in hydroponic culture. The second objective will be to apply the analytical methodology developed in Objective 1 to investigating the influence of mycorrhizae on root exudation and metal uptake from heavy metal contaminated soil (e.g. soils from McClellan Air Force Base, Sacramento, CA) in soil microcosms. These objectives will be met through the accomplishment of three tasks:

- (1) application of GC-MS and NMR techniques for comprehensive analysis of root exudate composition and biosynthesis over a range of metal concentrations for four micronutrients (Cu, Mn, Zn, and Ni) and two common metal pollutants (Cd and Al).
- (2) cell wall structure and fragment analysis of roots as a function of exposure to different concentrations of the selected metals.
- (3) soil microcosm experiments to investigate the effect(s) of soil microorganisms and mycorrhizae on (1) and (2).

Once root exudates or cell wall components that are involved in metal mobilization and/or transport are identified, it should be feasible to examine the metabolic control of their synthesis in future studies and to determine how microbial associations can affect this aspect of plant metabolism. Results from such research efforts should provide fundamental understanding of how soil-grown plants can be adapted for better performance in sequestering metal contaminants. An immediate benefit will be the development of methodology for rapid screening of plant varieties which may have enhanced metabolic capacity for metal mobilization and tolerance, and for examining enhancement of metal mobilization and uptake via plant breeding, manipulation of plant growth conditions, or microbial inoculation. Knowledge gained from this research should have direct applications to the design of plant-based remediation or restoration efforts.

## **Annual Progress Reports**

**1997 Progress Report**

**1998 Progress Report**

**1999 Progress Report**

**2000 Progress Report**

**2001 Progress Report**

# **Environmental Management Science Program Research in South Carolina**

## **University of South Carolina**

### **55205 – A Fundamental Study of Laser-Induced Breakdown Spectroscopy Using Fiber Optics for Remote Measurements of Trace Metals**

**Principal Investigator:** Dr. Scott R. Goode

**Problem Area:** Subsurface Contamination

Improved technologies are required by DOE for characterization and monitoring for site clean-up and waste processing applications. Especially needed are field deployable methods and devices of real-time monitoring to reduce dependency on laboratory analyses which are costly and time consuming. Improved sensors are needed for on-site analyses to provide real-time analytical capabilities for screening level and/or decision-quality data. Matrices of interest to the DOE are soils (or other solids), slurries, and aqueous and non-aqueous solutions.

Laser-induced breakdown spectroscopy (LIBS) is a useful method for determining the elemental composition of solids. This method has been recently reviewed and a number of different applications have been described. In the LIBS technique, a high-power pulsed laser is used to generate a plasma from the sample of interest. This phenomenon was first demonstrated in 1963 using a pulsed ruby laser. The elemental composition of the sample is accomplished by measuring the atomic emission from the atoms and ions in the plasma. There are many reports of the use of LIBS for measuring metals in solid substrates. There have also been LIBS investigations of aerosols, single particles, metals in solution including uranium, and even chlorinated species in solution. More recently, LIBS has been used for measuring Ba and Cr in soil using a fiber-optic cable. LIBS shows great potential for measuring metal contaminants in soils and on particles (e.g., stack emissions) based on their atomic emission in a laser-induced plasma. Another important application for this technique is the remote analysis of highly radioactive materials, such as the glasses produced by the Defense Waste Processing Facility. The use of fiber optics for both collection of the atomic emission and delivery of the laser to the sampling area could eliminate the need for sampling.

In this work we will study the time-evolution of the LIBS emission for different matrices to better understand how to optimize the signal. Also, we will investigate the use of fiber optics for laser delivery and signal collection, and the influence of the geometry of the fiber optic launch and collection probes to determine the effect on the signal-to-noise ratio (SNR). Finally, we will study the LIBS signal for different sample matrices as a function of excitation wavelength across a broad spectrum. A result of this study should be a determination of the optimal excitation and collection conditions and sampling times for metal contaminants in different matrices, and an understanding of the strengths and limitations of using fiber optics for LIBS sampling.

## **Annual Progress Reports**

[\*\*1997 Progress Report\*\*](#)

[\*\*1998 Progress Report\*\*](#)

[\*\*2000 Progress Report\*\*](#)

## Environmental Management Science Program Research in Tennessee

### Oak Ridge National Laboratory

#### 55267 – Containment of Toxic Metals and Radionuclides in Porous and Fractured Media: Optimizing Biogeochemical Reduction Versus Geochemical Oxidation

**Principal Investigator:** Dr. Phillip M. Jardine

**Problem Area:** Subsurface Contamination

The overall goal of the proposed research is to provide an improved understanding and predictive capability of the mechanisms that allow metal-reducing bacteria to be effective in the bioremediation of redox sensitive toxic metals and radionuclides. The study is motivated by the likelihood that subsurface metal-reducing bacteria can be stimulated to effectively alter the redox state of contaminants so that they are immobilized *in situ* for long time periods. The work described in this proposal will advance the technological and scientific needs associated with the long-term management of the enormous in-ground inventories of Cr, U, Tc, and Co present at numerous DOE installations throughout the country. The objectives of our project are to (1) develop an improved understanding and predictive capability of the rates and mechanisms controlling microbially mediated reduction of toxic metals and radionuclides and metals *in situ*, (2) quantify the impacts of hydrological and geochemical processes on the effectiveness of indigenous microorganisms to transform and immobilize radionuclides and metals *in situ*, (3) provide an improved understanding of the importance of microbial consortia interactions in the bacterial immobilization of radionuclides and toxic metals, and (4) determine intrinsic bioreduction rate parameters to improve our generic predictive capability of *in situ* microbially mediated metal reduction. Our approach involves a multiscale experimental and numerical endeavor that uses (1) undisturbed cores and a well-characterized, highly instrumented field facility for assessing biostimulation remedial strategies involving Cr(VI), U(VI), and Co(III)EDTA, (2) multiple tracer techniques designed to delineate the influence of coupled hydrological, geochemical, and microbial processes, (3) a novel microarray-based genomic technology for rapidly characterizing shifts in microbial community structure and activity, (4) sophisticated surface analysis techniques (x-ray absorption spectroscopy) for quantifying the distribution and chemical environment of the immobilized contaminants, and (5) next-generation, high-performance hydrobiogeochemistry modeling to assist the design and performance assessment of the proposed field scale experiment. The experimental and numerical results from this research will provide knowledge and information in previously unexplored areas of *in situ* biostimulation for metal and radionuclide immobilization to support EM's mission of long-term isolation and *in situ* remediation of contaminated environments. By unraveling the fundamental mechanisms controlling the microbially mediated reduction and immobilization of contaminants *in situ*, we provide an enhanced opportunity for successfully implementing biostimulation strategies at numerous DOE installations that are plagued with legacy waste. Further, this proposal combines DOE's commitment to environmental restoration with its commitment to major user facilities (SSRL, high-performance computing) and academic education.

### Annual Progress Reports

[1997 Progress Report](#)

[1998 Progress Report](#)

[1999 Progress Report](#)

# Environmental Management Science Program Research in Massachusetts

## Massachusetts Institute of Technology

### 55300 – 3-D Spectral IP Imaging: Non-Invasive Characterization of Contaminant Plumes

**Principal Investigator:** Dr. Frank Dale Morgan

**Problem Area:** Subsurface Contamination

The objective of this study is to develop a *noninvasive tomographic imaging technique*, based on the *spectral induced-polarization method*, to characterize the *in-situ distribution of organic and inorganic groundwater contaminants*. Recent advances in tomographic imaging, applied to d.c. resistivity data have made it possible and practical to obtain high-resolution 3-D images of sub surface resistivity structures. However, imaging of contaminant plumes with the d.c. resistivity method is only feasible in cases where the level of contamination is relatively high. Alternatively, the spectral IP response of rocks and soils, which arises from the polarization of an electrochemical surface phase at grain-solution boundaries, is very sensitive to even small amounts of contaminants. We plan to further develop our d.c. resistivity tomographic imaging algorithms to obtain a 3-D inversion code for spectral IP data. The resulting 3-D map of the spectral IP response can be used to characterize the subsurface chemical conditions. Laboratory studies will be conducted with the goal of obtaining a quantitative interpretation of the derived IP spectra in terms of the contaminant type and concentration. Lastly, field studies will be conducted at well-characterized field sites to test the overall performance of this integrated imaging method and to test new developments in field instrumentation. If this remote sensing method proves successful it will greatly enhance our ability to detect, identify, and map the distribution of contaminants in the subsurface. This technology will provide tremendous cost savings in terms of the number of boreholes that are necessary to characterize a contaminated site and it will be extremely useful in the characterization and monitoring of in-situ chemistry for remediation efforts.

## Annual Progress Reports

[1997 Progress Report](#)

[1998 Progress Report](#)

[2000 Progress Report](#)

# **Environmental Management Science Program Research in California**

## **Lawrence Berkeley National Laboratory**

### **55343 – Enzyme Engineering for Biodegradation of Chlorinated Organic Pollutants**

**Principal Investigator:** Dr. Peter G. Schultz

**Problem Area:** Subsurface Contamination

Halogenated organic compounds have had widespread use as fungicides, herbicides, insecticides, algacides, plasticizers, solvents, hydraulic fluids, refrigerants and intermediates for chemical syntheses. As a result, they constitute one of the largest groups of environmental pollutants. Chlorinated organic compounds comprise the largest fraction of these materials, having been synthesized by large scale processes over the past few decades. Their ubiquitous use and distribution in our ecosystem has raised concern over their possible effects on public health and the environment.

The biodegradation potential of halogenated compounds is difficult and not well understood. Biological cleavage of carbon-halide bonds can be achieved by either enzymatic or biocatalytic dehalogenation or by spontaneous chemical dehalogenation of unstable intermediates. This research involves the protein engineering of existing enzymes and the "creation" of new enzymes (catalytic antibodies) with enhanced dechlorination capability for a wide variety of chlorinated organic pollutants. These enzymes could be used as such or could be inserted into microorganisms designed for high activity in contaminated environments.

Development of antibodies that catalyze the hydrolysis of halogenated aromatics will be carried out through a combination of chemical and genetic approaches. Haptens will be developed to generate antibodies that stabilize the transition state for hydrolysis of halogenated nitroaromatics. We will then randomize the variable regions of the antibodies and screen for antibodies with enhanced catalytic properties. If successful such an approach could be generalized and might allow one to tailor the specificity of a bioremediation catalyst for a given synthetic halogenated aromatic using the machinery of the immune system.

We will also attempt to clone, express, purify and to determine the structure and chemical mechanism of a known detoxifying enzyme, dechlorinating dehalogenase. In addition, knowledge gained from such studies will be used to redesign the dehalogenase for the purpose of expanding its biodegradative potential to include environmental pollutants that are currently non-biodegradable.

## **Annual Progress Reports**

**1997 Progress Report**

**1998 Progress Report**



## **Environmental Management Science Program Research in New Mexico**

### **Sandia National Laboratories – New Mexico**

#### **55395 – Physics of DNAPL Migrations and Remediation in the Presence of Heterogeneities**

**Principal Investigator:** Dr. Stephen H. Conrad

**Problem Area:** Subsurface Contamination

We will conduct well-controlled laboratory experiments to better understand the physics of DNAPL migration and remediation in the presence of heterogeneities. These experiments will be used to develop and test an upscaled percolation model, a new approach for modeling DNAPL migration. Finally, numerical simulators under current use in evaluating remediation techniques will be compared against our remediation experiments. We will make use of our unique experimental capabilities in the Subsurface Flow and Transport Processes Laboratory at Sandia to conduct controlled, systematic, repeatable experiments that first consider the physics of DNAPL migration in initially water saturated, heterogeneous porous media and then evaluate the efficacy of a suite of promising remediation techniques for remediating DNAPLs from heterogeneous aquifers. The results of the migration experiments will be used to test and continue development of new modeling approaches based on upscaled percolation theory developed by us and by collaborators. In addition, the results of the remediation experiments will be used to test, for the first time, within heterogeneous media the quantitative performance of remediation design codes (two-phase flow codes that incorporate compositional models).

### **Annual Progress Reports**

[\*\*1997 Progress Report\*\*](#)

[\*\*1998 Progress Report\*\*](#)

[\*\*1999 Progress Report\*\*](#)

## **Environmental Management Science Program Research in Texas**

### **Rice University**

#### **60115 – Advanced High Resolution Seismic Imaging, Material Properties Estimation and Full Wavefield Inversion for the Shallow Subsurface**

**Principal Investigator:** Dr. Alan Levander

**Problem Area:** Subsurface Contamination

We propose to develop and test an integrated suite of imaging and inverse techniques appropriate to the range of wave propagation regimes customarily recorded in shallow seismic surveys. These techniques will address the extreme physical conditions found in the shallow environment, and thereby significantly advance the ability of shallow seismic investigations to produce high fidelity structural and material property maps of the subsurface. High resolution subsurface material properties maps are essential for characterizing the geometry of aquifers, aquicludes, and other fluid pathways, and therefore are essential for environmental remediation efforts.

We will apply these methods to a number of high resolution profiles we have acquired and are proposing to acquire at sites with different near surface properties, including two active environmental remediation sites. The methods to be developed represent basic research in seismic imaging, and include advanced wavefield imaging using pre-critical to post-critical energy, velocity estimation and reflector focusing, and wavefield inversion techniques appropriate for imaging and estimating the material properties of the highly heterogeneous near surface environment. The research will build on the PIs' previous research developing seismic imaging and inversion methods tailored for petroleum exploration and crustal investigations. At all stages of the data processing we propose to exploit the entire wavefields commonly recorded (and often overlapping in time, space, frequency, and phase velocity) but customarily processed and interpreted independently in high resolution surveys.

### **Annual Progress Reports**

**1998 Progress Report**

**1999 Progress Report**

**2000 Progress Report**

# Environmental Management Science Program Research in Oregon

## Oregon State University

### 60158 – Development of Radon-222 as a Natural Tracer for Monitoring the Remediation of NAPL Contamination in the Subsurface

**Principal Investigator:** Dr. Lewis Semprini

**Problem Area:** Subsurface Contamination

One of the major obstacles preventing cost-effective cleanup of many DOE sites is the current inability to accurately locate and quantify residual nonaqueous phase liquid (NAPL) contamination. The recently developed *natural radon tracer method* has the potential to provide a rapid, low-cost, nondestructive, and noninvasive method for routine use in quantifying residual NAPL in the subsurface. The method is based on detecting changes in radon concentration in groundwater samples collected from existing monitoring wells. In the subsurface, radon-222 (radon) is produced by the decay of naturally occurring radium-226 contained in the mineral fraction of aquifer solids. In groundwater radon occurs as a dissolved gas, with a half-life of 3.83 days. In the absence of NAPL, radon concentrations quickly reach a maximum value that is determined by the mineral composition of the aquifer solids, which controls the rate of radon emanation. In the presence of NAPL, however, radon concentrations are substantially reduced due to the preferential partitioning of radon into the organic NAPL phase. Moreover, the reduction in radon concentration is quantitatively correlated with residual NAPL saturation. Thus, by measuring radon concentrations in a number of wells it is possible to identify those locations where NAPL is likely present and to quantify residual NAPL saturation in each location.

In an exploratory grant funded by the DOE through the Western Region Hazardous Substance Center of the EPA, the feasibility of the radon method was demonstrated by Dr. Semprini using a combination of laboratory studies and numerical modeling. The method has also been successfully used to detect residual NAPL in a controlled release experiment and to identify possible NAPL locations at a DOE field site. The research will focus on the fundamental processes governing radon emanation, partitioning, and transport in heterogeneous subsurface environments and the use of the method to identify and quantify residual NAPL saturations at a DOE site undergoing active remediation to remove NAPL.

The specific research objectives are:

1. to determine the dependence of radon emanation from natural aquifer solids on the composition and properties of fluids filling the pore space,
2. to determine radon NAPL: water partition coefficients for a broad range of LNAPLs and DNAPLS of environmental concern,
3. to quantify relations between radon emanation and partitioning and regional flow and transport in heterogeneous subsurface materials before and during NAPL remediation.
4. to test the feasibility of the radon method to identify and quantify residual NAPL during site remediation, and
5. to conduct numerical simulations to extend the applicability of laboratory and field results to a wider range of DOE sites.

The research combines small-scale laboratory studies, intermediate-scale laboratory studies in unique physical aquifer models, field studies at a DOE site undergoing active NAPL remediation, and numerical simulations to extend the range of applicability of the laboratory and field results to a wider range of NAPL contamination problems at DOE sites.

## **Annual Progress Reports**

**1998 Progress Report**

**1999 Progress Report**

**2002 Progress Report**

## **Environmental Management Science Program Research in Tennessee**

### **Oak Ridge National Laboratory**

#### **60197 – Microsensors for In-Situ Chemical, Physical, & Radiological Characterization Mixed Waste**

**Principal Investigator:** Dr. Thomas G. Thundat

**Problem Area:** Subsurface Contamination

A widespread need exists for portable, real-time, in-situ chemical, physical, and radiological sensors in characterization of mixed waste, groundwater, contaminated soils and process streams. None of the currently available technologies offer a clear path to the development of sensors that are miniature, cost-effective, selective, highly sensitive with a wide dynamic range, and with the ability to work in air or liquid while providing chemical, physical, and radiological information. We propose an innovative single-sensor platform approach that is based on the recently discovered extreme sensitivity of microcantilever sensing using adsorption-induced forces.

The objective of this research program is to gain a better understanding of the basic mechanism of adsorption-induced differential surface stress variation and to use this novel idea for developing sophisticated microsensor concepts for sensing in liquids. As a demonstration we will develop: (i) chemically specific microsensors by coupling surface modification chemistry with molecular recognition agents for identification of inorganic species found in groundwater, (ii) coating techniques that will enable operation in corrosive, and high ionic strength environment, and (iii) microcantilevers for assessing local radioisotope content based on radiation damage.

This new multipurpose sensor technology offers the potential to provide real-time, in-situ characterization of the chemical, physical, and radiological properties of groundwater, contaminated soils and process streams. The advantage of this approach is that once the basic technique is developed, it can be the basis for a universal sensor platform for many DOE needs such as the chemical, physical, and radiological characterization of tank waste, monitoring of environmental cleanup processes, and the detection of emitted gases from incinerators and waste vitrification plants.

### **Annual Progress Reports**

**1998 Progress Report**

**1999 Progress Report**

**2000 Progress Report**

**2001 Progress Report**

# **Environmental Management Science Program Research in Kansas**

## **The University of Kansas**

### **60199 – Automating Shallow Seismic Imaging**

**Principal Investigator:** Dr. Don W. Steeples

**Problem Area:** Subsurface Contamination

The research we are proposing as a continuation of our EMSP contribution is designed to develop ultrashallow seismic imaging into a cost-effective method that could be applicable to DOE facilities. The objective of the research proposed here is to develop and demonstrate the use of a cost-effective automated method of conducting shallow seismic surveys. We emphasize that this approach represents a significant departure from conventional seismic-survey field procedures. Our initial testing suggests that large numbers of geophones can be placed automatically by a mechanical device, which could make the application of shallow seismic reflection (SSR) considerably faster and cheaper. The imaging results obtained using the proposed automated seismic methods will be compared with results obtained using classical seismic techniques as well as GPR surveys, and, in the third year of the proposed research, demonstration surveys at one or more DOE facilities will be performed. The techniques proposed here are not limited to shallow seismic reflection methods but would also be capable of collecting data for seismic-refraction and possibly for surface-wave studies. Although the research we propose falls primarily into the field of seismology, some ground penetrating radar (GPR) data will be collected at a very small additional incremental cost for comparison and quality-control purposes.

## **Annual Progress Reports**

**1998 Progress Report**

**1999 Progress Report**

**2000 Progress Report**

# **Environmental Management Science Program Research in California**

## **Lawrence Berkeley National Laboratory**

### **60328 – High Frequency Electromagnetic Impedance Measurements for Characterization, Monitoring and Verification Efforts**

**Principal Investigator:** Dr. Ki Ha Lee

**Problem Area:** Subsurface Contamination

We propose to continue development of high-frequency impedance (HFI) methodology utilizing a window in the electromagnetic (EM) spectrum from 1.0 MHz to 100 MHz. This window, located between GPR and low-frequency induction techniques, has not been used to non-invasively investigate the upper few meters of the ground for environmental applications. Modeling and physical parameter studies confirm that impedance measurements in this frequency band can yield high-resolution mapping of electrical conductivity as well as the permittivity of near surface formations. In principle the impedance method we propose is free of source coupling for plane waves, so that the ensuing data analysis tends to be much simpler.

The proposed research plan consists of three tasks: 1) continued development and completion of high-frequency field measurement techniques, 2) construction and delivery of a field-hardened prototype HFI system, and 3) data processing, analysis, and interpretation. The proof-of-concept for the HFI system has been demonstrated in the first phase of the research program (1997 through 2000). Construction of a mobile HFI field system can be accomplished using off-the-shelf instrumentation and commercially available components, but research will be continued to develop better high-frequency sensors using innovative designs. Development of an analysis package for processing and interpretation of high-frequency data is also an essential part of the proposed work. Towards the end of the project, the prototype system will be capable of real-time mapping of the electrical conductivity and permittivity using simultaneous inversion in one dimension. Feasibility for implementing higher-dimensional analysis package in field operation will be critically evaluated.

## **Annual Progress Reports**

**1998 Progress Report**

**1999 Progress Report**

**2000 Progress Report**

# **Environmental Management Science Program Research in Washington**

## **Pacific Northwest National Laboratory**

### **60355 – Mineral Surface Processes Responsible for the Decreased Retardation (or Enhanced Mobilization) of $^{137}\text{Cs}$ from HLW Tank Discharges**

**Principal Investigator:** Dr. John M Zachara

**Problem Area:** Subsurface Contamination

High level wastes (HLW) were generated during the extraction of Pu and other elements from irradiated uranium fuels. Most of the HLW remain stored at the Hanford site in 177 massive underground storage tanks. Sixty-seven of these tanks have leaked discharging ca. 1 million gallons of waste to the subsurface containing 1 million Ci of radiation, most of which is  $^{137}\text{Cs}$ . Although strongly sorbed by the micaceous fraction of the underlying sediments,  $^{137}\text{Cs}^+$  has migrated significant distances below some tanks leading to concern that it may reach groundwater.

This project will investigate the geochemistry of  $\text{Cs}^+$  adsorption under conditions relevant to HLW tank releases. Emphasis is placed on Hanford REDOX wastes, as field evidence suggests that the chemical composition of these promote enhanced subsurface Cs migration. The central research tenets are that the high Na concentrations in the HLW will suppress all but the most selective Cs sorption sites that occur on the frayed edges of micaceous particles (FES), and that FES may be chemically altered by hydroxide and aluminate in HLW.

The research integrates studies of ion exchange thermodynamics on the FES, with high resolution surface microscopies (HRTEM, AFM, TOF-SIMS) and molecular spectroscopy (NMR, EXAFS) to probe the structure of FES in Hanford sediments and how the chemical environment of sorbed Cs changes when HLW supernatants promote sorbent dissolution and the precipitation of new phases. Our goal is to develop field relevant knowledge to improve transport calculations of Cs beneath the tank farms and provide needed insights for long term decision making pertaining to performance/risk assessment and site-restoration. Specifically, the research will:

- Identify how the macroscopic sorption behavior of Cs on the micaceous fraction of Hanford sediments changes after contact with HLW simulants as a function of temperature and chemical parameters.
- Reconcile observed changes in Cs sorption chemistry with microscopic and molecular changes in the site distribution, chemistry, mineralogy, and morphology/structure of highly selective sorption sites in the micaceous fraction.
- Integrate mass action solution exchange measurements with microscopic characterization of the surface structure and chemistry of the selective sorbent phase to yield a multi-component exchange model for prediction of Cs sorption.

## **Annual Progress Reports**

[1998 Progress Report](#)

[1999 Progress Report](#)

[2000 Progress Report](#)



# Environmental Management Science Program Research in Ohio

## University of Cincinnati

### 70010 – Spectroelectrochemical Sensor for Technetium Applicable to the Vadose Zone

**Principal Investigator:** William R. Heineman

**Problem Area:** Subsurface Contamination

The general aim of our work funded by EMSP is the design and implementation of a new sensor technology that offers unprecedented levels of specificity needed for analysis of the complex chemical mixtures found at DOE sites nationwide. The specific goal of this proposal is the development of a sensor for technetium (Tc) that is applicable to characterizing and monitoring the Vadose Zone and associated subsurface water at the Hanford site. Subsurface contamination by Tc is of particular concern for two reasons: the extremely long lifetime of its most common isotope  $^{99}\text{Tc}$  (half-life =  $2 \times 10^5$  years) and the fast migration in soils that its most common chemical form, pertechnetate ( $\text{TcO}_4^-$ ) exhibits. The sensor will be capable of determining the concentration of Tc in various chemical forms including  $\text{TcO}_4^-$  and lower oxidation states of Tc that are complexed with organic ligands. The primary focus of this proposal is  $\text{TcO}_4^-$ , which is considered to be the dominant species in the Vadose Zone and subsurface water. The sensor will have the capability for on-site monitoring, either by immersion in subsurface water for continuous monitoring or for the immediate analysis of collected samples.

The concept for this  $\text{TcO}_4^-$  sensor is innovative and represents a breakthrough in sensor technology. The sensor combines three modes of selectivity (electrochemistry, spectroscopy, and selective partitioning) into a single sensor to substantially improve selectivity. The sensor will consist of a basic spectroelectrochemical configuration that we have developed under our existing EMSP grant: a waveguide with an optically transparent electrode that is coated with a thin chemically selective film. Proof of concept of this spectroelectrochemical sensor has been demonstrated under our existing EMSP grant for the determination of ferrocyanide in Hanford tank waste. A prototype sensor has been developed and is currently undergoing testing using In-Farm and U-Plant Hanford simulated wastes. The key to adapting this generic sensor to detect  $\text{TcO}_4^-$  lies in the development of unique chemistry within the chemically selective film. This film will be developed so that  $\text{TcO}_4^-$  in the sample will partition into it by electrostatic attraction. Once  $\text{TcO}_4^-$  is loaded into the film, it is electrochemically converted into a Tc coordination compound that gives a strong optical signal associated with an electrochemical reduction/oxidation process. The magnitude of the absorbance change accompanying the electrochemical modulation of this coordination compound will quantitate the concentration of Tc within the film, which is proportional to the concentration of  $\text{TcO}_4^-$  in the sample.

#### **The research plan will incorporate the following specific tasks:**

*Choice of materials and fabrication of the chemically selective layer that initially traps  $\text{TcO}_4^-$ .* An appropriate polymer for partitioning  $\text{TcO}_4^-$  into the film will be chosen.

*Choice of ligand that binds reduced Tc species within the chemically selective layer.* Several ligands for binding with reduced Tc species to form a coordination compound will be evaluated for the requisite electrochemical and spectral properties.

*Co-immobilization of  $\text{TcO}_4^-$  trapping polymer and ligand on the sensor platform.* The most efficacious ligand(s) and polymer(s) will be co-immobilized as a film on the sensor platform to demonstrate the concept in conjunction with the spectroelectrochemical sensor.

*Characterization and optimization of sensor performance on  $\text{ReO}_4^-$  and  $\text{TcO}_4^-$  standards* with respect to the following performance characteristics: detection limit, selectivity, reversibility, and ruggedness.

*Characterization and optimization of sensor performance on samples from the Vadose Zone and subsurface water at Hanford.* Samples simulating the Vadose Zone will be analyzed with the sensor in addition to actual samples from the Vadose Zone and associated subsurface water.

*Demonstration of the extension of the sensor design to other chemical forms of technetium.* The applicability of the sensor concept to the detection of technetium in lower oxidation states that are coordinated with organic ligands will be demonstrated.

This project will involve a collaboration between scientists at the University of Cincinnati (UC) and the Pacific Northwest National Laboratory (PNNL).

## **Annual Progress Reports**

**2000 Progress Report**

**2001 Progress Report**

**2002 Progress Report**

# **Environmental Management Science Program Research in Vermont**

## **New England Research, Inc.**

### **70012 – Complex Electrical Resistivity for Monitoring DNAPL Contamination**

**Principal Investigator:** Stephen R. Brown

**Problem Area:** Subsurface Contamination

We propose to develop new practical complex resistivity field measurement techniques for pollution characterization and monitoring. For this purpose we will document the detectability of clay-organic interactions with geophysical measurements in the laboratory, develop further understanding of the underlying physical and chemical mechanisms, and then apply these observations to develop field techniques to monitor the remediation of organic pollutants. This proposed work is driven by the following simple hypothesis: as organic compounds are removed (e.g., biodegraded or extracted through engineered remediation) the complex resistivity will change according to the new chemical make-up of the soil/groundwater system. Thus complex resistivity measurements can be used as an effective monitoring tool to indicate the progress of remediation activities.

A field implementation of the complex resistivity technique targeted at pollutant characterization would provide a quick and inexpensive means of monitoring the progress of the breakdown of the pollutants in-situ without intervention and without disturbing the process. This technique would be implemented, for example, through the emplacement of standard 2-D arrays of contacting electrodes combined with complex resistivity measurement equipment, techniques, and data analysis methods. These data would be used to create spatial images of the pollution location and concentration in the subsurface. Successive images through time would be subtracted to monitor the remediation efforts.

To accomplish these goals, we will: (1) perform laboratory studies to identify complex resistivity signatures of the most important components of DNAPL's; (2) evaluate the signal and noise levels in the field; (3) identify distinguishing characteristics of complex resistivity contaminant signatures and develop algorithms to identify them; (4) perform parameter studies of complex resistivity signature changes among natural rocks, soils, fluid chemistry, and saturation levels; (5) evaluate the ability of standard electrical geophysics field equipment to measure these effects. If standard equipment is unsuitable, develop prototype frequency-sweeping portable equipment with modern phase lock-in electronics to give field measurements the noise immunity required to reliably discern the low-level signals; (6) develop a broad-band pulse method for rapid data acquisition and scoping measurements; and (7) develop measurement techniques and software for complex resistivity imaging from arrays of surface electrodes.

## **Annual Progress Report**

[\*\*2001 Progress Report\*\*](#)

[\*\*2002 Progress Report\*\*](#)

# Environmental Management Science Program Research in New York

## Clarkson University

### **70035 – DNAPL Surface Chemistry: Its Impact on DNAPL Distribution in the Vadose Zone and its manipulation to Enhance Remediation**

**Principal Investigator:** Susan E. Powers

**Problem Area:** Subsurface Contamination

The remediation of DNAPLs in subsurface environments is often limited by the heterogeneous distribution of the organic fluid. The fraction of DNAPL that is in the high conductivity regions of the subsurface can often be recovered relatively easily, although DNAPL in lower conductivity regions is much more difficult to extract, either through direct pumping or remediation measures based on interface mass transfer. The distribution of DNAPL within the vadose zone is affected by a complex interplay of heterogeneities in the porous matrix and the interfacial properties defining the interactions among all fluid and solid phases.

The primary hypothesis of this work is that surface-active chemicals and/or microorganisms present in the unsaturated zone can significantly alter the interfacial phenomena governing the migration of DNAPLs, thereby affecting the accessibility of a DNAPL during remediation efforts. The surface-active materials are present in complex NAPL mixtures and are produced through microbial metabolic processes. The overall goal of this proposed research is to understand the role of and changes in interfacial phenomena on the accessibility of DNAPL in the vadose zone. Results of this effort could potentially be used to increase the accessibility and, therefore, the recovery of DNAPL during vapor extraction or other vadose zone remediation efforts. Four objectives have been defined to meet this overall goal.

Understand and quantify the interfacial properties of DNAPLs in response to biological activity or the presence of surface-active constituents within the DNAPL mixture or aqueous phase.

Identify conditions under which CT and TCE co-metabolizing cultures affect interfacial properties through the production of surface-active materials or by adhering at NAPL interfaces.

Quantify the net effects associated with DNAPL surface chemistry on phenomena governing multiphase flow in the unsaturated zone and remediation efforts.

Examine the role of surface chemistry on the distribution of DNAPL in a field setting.

A multi-task approach involving experimental measurements at both laboratory and field scales has been designed to meet the objectives of this research. Materials for this research have been chosen to be applicable to vadose zone contamination problems at the Savannah River (SRS) and Hanford facilities. Initial stages of the research will focus on well-characterized materials with a shift to site-specific media as the processes are understood. The research proposed herein offers a unique opportunity to develop our fundamental understanding of the fate of DNAPLs in the vadose zone through both laboratory scale testing and evaluation of extensive field samples collected at SRS. Field work at the SRS provides an opportunity to study the distribution of DNAPL following releases of both fresh solvent and spent solvent that have occurred at different locations within a single geologic setting under roughly comparable initial, pristine conditions. The field work will provide a detailed assessment of the distribution of DNAPL in the subsurface as a function of DNAPL composition, mineral characterization, and heterogeneous grain size distribution. Concurrent laboratory testing will provide an understanding of the fundamental mechanisms governing these distributions. A modeling component of the proposed research will increase our understanding of fundamental mechanisms, provide parameters for constitutive relationships, and enable assessment of the significance of these factors in larger scale heterogeneous systems. Coupling these results will verify the significance of the various variables tested leading to the identification of conditions that may increase the efficacy of vadose zone remediation efforts.

The research effort will be carried out with a collaborative effort between principal investigators at Clarkson University and the Westinghouse Savannah River Company (WSRC). Clarkson personnel will lead the laboratory-testing phase of the research associated with objectives one through three. The field activities and characterization of the soil borings collected at SRS will be the responsibility of personnel at WSRC. Two graduate students will be funded through this project, they will also have an opportunity to participate in field activities and associated analysis of soil borings in addition to their laboratory and modeling efforts at Clarkson.

## **Annual Progress Report**

**2001 Progress Report**

**2002 Progress Report**

# **Environmental Management Science Program Research in Illinois**

## **University of Illinois**

### **70045 – Investigation of Pore-Scale Processes which Affect Soil Vapor Extraction**

**Principal Investigator:** Albert Valocchi

**Problem Area:** Subsurface Contamination

Dense nonaqueous phase liquid (DNAPL) contamination in the vadose zone is a significant problem at Department of Energy sites. According to a 1992 report (DOE, 1992), chemicals commonly associated with DNAPLs (i.e., chlorinated hydrocarbons) were the second most commonly identified contaminants in soils and sediments at 18 DOE facilities. Soil vapor extraction (SVE) is commonly used to remediate DNAPLs from the vadose zone. In most cases, a period of high recovery has been followed by a sustained period of low recovery. This behavior has been attributed to multiple processes including slow interphase mass transfer, retarded vapor phase transport, and diffusion from unswept zones of low permeability.

Prior attempts to uncouple and quantify these processes have relied on column experiments, where the effluent concentration was monitored under different conditions in an effort to quantify the contributions from a single process. In real porous media these processes occur simultaneously and are inter-related. Further, the contribution from each of these processes varies at the pore scale and with time. For example, if dry vapor is pulled into the ground during SVE, the soil matrix may “dry out” along the vapor phase flow path, resulting in changes to the mass transfer mechanisms which control SVE. This is especially important in arid environments like Hanford, where SVE is being used to remove carbon tetrachloride from the vadose zone.

Research proposed here aims to determine the pore-scale processes which limit the removal of DNAPL components in heterogeneous porous media during SVE. The specific objectives of this research are to: 1) determine the effect of unswept zones on DNAPL removal during SVE, 2) determine the effect of retarded vapor phase transport on DNAPL removal during SVE, and 3) determine the effect of interphase mass transfer on DNAPL removal during SVE, all as a function of changing moisture and DNAPL content.

To fulfill these objectives we propose to use magnetic resonance imaging (MRI) to observe and quantify the location and size of individual pores containing DNAPL, water, and vapor in flow through columns filled with model and natural sediments. MRI is unique because it is non-destructive, allowing three-dimensional images to be taken of the phases within actual pores as a function of space and time. Imaging results will be used in conjunction with innovative modeling techniques to develop spatially and temporally dependent constitutive relations which describe the transient distribution of phases inside a column experiment. These constitutive relations will be incorporated into a site-scale transport model to evaluate how the different processes affect SVE performance in practical applications. This will allow decision makers to better assess the risk associated with vadose zone contamination and the effectiveness of SVE at hazardous waste sites.

## **Annual Progress Report**

**2001 Progress Report**

**2002 Progress Report**

# Environmental Management Science Program Research in South Carolina

## University of South Carolina

### 70050 – Novel Optical Detection Schemes for In-Situ Mapping of Volatile Organochlorides in the Vadose Zone

**Principal Investigator:** Dr. S. Michael Angel

**Problem Area:** Subsurface Contamination

Improved technologies are required by DOE for characterization and monitoring for site clean-up and waste processing applications. Especially needed are field deployable methods and devices for real-time monitoring to reduce dependency on laboratory analyses which are costly and time consuming. Improved sensing capabilities are needed for on-site analyses to provide real-time analytical capabilities for screening level and/or decision-quality data. Matrices of interest to the DOE are soils (or other solids), slurries, and aqueous and non-aqueous solutions. In-situ methods have been demonstrated for identifying high concentrations of organic liquids (e.g., Raman spectroscopy) and low concentrations of a few types of organic molecules (e.g., UV fluorescence and DUVAS), as well as a few selected organic molecules (e.g., sensors) at low concentrations. However, currently there is no method for measuring low levels of organic vapors of the type that would be indicative of subsurface contamination in the vadose zone. The proposed research focuses specifically on a method, resonance-enhanced multi-photon ionization - REMPI, for measuring organic solvents in a soil matrix by detecting organic vapors in the vicinity of a NAPL. We propose using this technique in combination with Raman spectroscopy thus allowing organic contaminants to be measured and identified over a very wide range of concentrations. Our proposed REMPI studies are different from current approaches in that we will use a visible laser for excitation rather than a UV laser, as is used by other groups, to reduce the cost and complexity of the instrumentation, and make the system more robust and reliable. Furthermore, visible wavelengths are more compatible with existing fiber-optic probes and will make it easier to make field measurements using long fiber cables.

A highly multidisciplinary group of scientists has been assembled for this project. Angel (analytical chemist with experience with sensors and probe designs), Gribb (civil engineer with expertise in hydraulic measurements, cone penetrometer measurements and soil column design), Colston and Brown (biophysics, electrical engineering with expertise in OPO measurements, cone penetrometer instrumentation, and subsurface measurements using fiber optics). Furthermore, experts in cone penetrometer experiments will help in the field studies. All groups will be working on the same topics but in this project we combine fundamental research (at USC) with technology development and applications (at LLNL). The highly multidisciplinary nature of this research team will improve our chances of successfully completing the project with the generation of technology that can be used by DOE in support of subsurface remediation efforts.

## Annual Progress Report

### 2001 Progress Report

# **Environmental Management Science Program Research in Wyoming**

## **University of Wyoming**

### **70052 – Material property Estimation for Direct Detection of DNAPL using Integrated Ground-Penetrating Radar Velocity, Imaging, and Attribute Analysis**

**Principal Investigator:** John Bradford

**Problem Area:** Subsurface Contamination

We propose to test and develop a suite of methodologies for direct detection of pooled and residual DNAPLs from surface ground-penetrating radar (GPR) data. This is a new, quantitative approach to the analysis of GPR data in which we determine material properties remotely by quantifying signal characteristics such as propagation velocity and waveform attributes including amplitude, frequency content, and phase. With careful consideration of the physics governing electromagnetic (EM) wave propagation, these properties can be extracted from GPR data to characterize variations in electric properties. Many DNAPLs, including chlorinated solvents, have much lower dielectric permittivity and conductivity than water. A contrast in electric properties is induced when DNAPL displaces water in the sediment column resulting in an anomalous GPR attribute signature. The attribute signature can be exploited for remote DNAPL detection.

In our approach, we focus on three aspects of reflected wave behavior - propagation velocity, frequency dependent attenuation, and amplitude variation with offset. Velocity analysis provides a direct estimate of dielectric permittivity, attenuation analysis is used to identify variation in conductivity, and AVO behavior is used to quantify the dielectric permittivity ratio at a reflecting boundary. Attribute analysis is integrated with sophisticated signal processing methodologies, not commonly applied in GPR investigation, which dramatically improve image resolution and spatial accuracy. We have completed much of the preliminary work to include theoretical development, numerical and physical modeling studies, and initial development of attenuation and AVO attribute extraction algorithms.

The next step in development of these methods is rigorous field testing under a variety of hydrogeologic conditions. To this end, the focus of our proposed work is field investigation. We have identified a number of sites suitable for controlled GPR investigation including the Hanford Site, WA, and four facilities designated as National Environmental Technology Test Sites (Dover AFB, DE; McClelland AFB, CA; Port Hueneme, CA; Wurtsmith AFB, CA). We propose to conduct a series of controlled and uncontrolled GPR experiments over known NAPL source areas at these sites. An integral part of data analysis will be continued development of attribute extraction algorithms. These algorithms will include methods for automated attribute extraction and material property estimation based on the physics of EM wave propagation.

Previous GPR NAPL detection studies have relied on minimal data processing and qualitative interpretation of subsurface profiles. Our approach combines sophisticated processing methodology with quantitative attribute analysis and material property estimation. The proposed research will lead to more efficient processing, reliable, accurate interpretations, and detection of subtle variations that are difficult or impossible to identify through qualitative interpretation alone. Implementation of these methodologies will be a significant advance in GPR research and in meeting DOE's need for reliable in-situ characterization of DNAPL contamination.

## **Annual Progress Report**

### **2001 Progress Report**

### **2002 Progress Report**



# Environmental Management Science Program Research in Georgia

## University of Georgia

### 70054 – Phytoremediation of Ionic and Methyl Mercury Pollution

**Principal Investigator:** Richard B. Meagher

**Problem Area:** Subsurface Contamination

Our long-term goal is to enable highly productive plant species to extract, resist, detoxify, and/or sequester toxic heavy metal pollutants as an environmentally friendly alternative to physical remediation methods. We have focused our research on the phytoremediation of soil and water-borne ionic and methylmercury. Mercury pollution is a serious world-wide problem affecting the health of human and wild-life populations. Methylmercury, produced by native bacteria at mercury-contaminated wetland sites, is a particularly serious problem due to its extreme toxicity and efficient biomagnification in the food chain. We engineered several plant species to express two bacterial genes, *merB* and *merA*, and they acquired remarkable properties for mercury remediation. 1) Transgenic plants expressing *merB* extract methylmercury from their growth substrate and degrade it to less-toxic ionic mercury. They grow on concentrations of methylmercury that kill normal plants. 2) Transgenic plants expressing *merA* extract and electrochemically reduce toxic, reactive ionic mercury to much less toxic and volatile metallic mercury and transpire it from their leaves. This metal transformation is driven by the powerful photosynthetic reducing capacity of higher plants. *MerA* plants grown vigorously on levels of ionic mercury that kill control plants. Plants expressing both *merB* and *merA* degrade methylmercury and volatilize metallic mercury. Our work demonstrates that native trees, shrubs, and grasses can be engineered to remediate the most abundant toxic mercury pollutants. Building on these data our working hypothesis for the next grant period is that transgenic plants expressing the bacterial *merB* and *merA* genes will (a) remove mercury from polluted soil and water and (b) prevent methylmercury from entering the food chain. Our specific aims center on understanding the mechanisms by which plants process the various forms of mercury and transpire mercury vapor. This information will allow us to improve the design of our current phytoremediation strategies. As an alternative to volatilizing mercury, we are using several new genes to construct plants that will hyperaccumulate mercury in above-ground tissues for later harvest. The Department of Energy's Oak Ridge National Laboratory and Brookhaven National Laboratory have sites with significant levels of mercury contamination that could be cleaned by applying the scientific discoveries and new phytoremediation technologies described in this proposal. The knowledge and expertise gained by engineering plants to hyperaccumulate mercury can be applied to the remediation of other heavy pollutants (e.g., arsenic, cesium, cadmium, chromium, lead, strontium, technetium, uranium) found at several DOE facilities.

## Annual Progress Reports

[2000 Progress Report](#)

[2001 Progress Report](#)

# Environmental Management Science Program Research in California

## Stanford University

### 70063 – Biodegradation of Chlorinated Solvents: Reactions Near DNAPL and Enzyme Function

**Principal Investigator:** Dr. Perry L. McCarty

**Problem Area:** Subsurface Contamination

Chlorinated solvents are among the most common organic chemical groundwater contaminants at DOE sites, as well as at DOD and industrial facilities. Included are the solvents trichloroethene (TCE), tetrachloroethene (PCE), and carbon tetrachloride (CT). Commonly these contaminants occur as dense non aqueous phase liquids (DNAPLs) that continue to contaminate groundwater as it moves through the DNAPL location. Also, commonly, these contaminants are associated with other contaminants of concern. An example is the Hanford site where nitrates, tritium, and carbon tetrachloride co-mingle in significant plumes. The objective of this study is to obtain basic information on processes affecting the in situ biodegradation of the above chlorinated solvents and their degradation daughter products, especially near the DNAPL source where concentrations are exceptionally high. Here, we have found anaerobic biological processes provide the best opportunity for efficient in situ biodegradation because the high concentrations of solvents and daughter products tend to be inhibitory to other microorganisms, such as methanogens, that compete for electron donor that may be added to enhance this process. We have laboratory cultures that are capable of degrading saturation concentrations of PCE, and are cooperating with DuPont Chemical Corporation, who has several mixed cultures, as well as molecular probes, that will be useful in this study. The study will be conducted in three separate phases. In the first, the kinetics of chlorinated solvent biodegradation at or near saturation concentrations will be investigated. Important here is the potential for inhibition by individual chlorinated solvents and end products, as well as those of potential co-contaminants. The second phase is to develop a better understanding of the underlying biochemical processes involved in key enzymatic reactions, such as the dehalogenation of vinyl chloride. From these studies, molecular probes that can detect the presence and activity of dehalogenating enzyme activity will be developed for field application. The third phase is concerned with obtaining better basic knowledge of a highly unique denitrifying bacteria (*Pseudomonas stutzeri* strain KC) that degrades carbon tetrachloride without producing chloroform as a hazardous intermediate. We have successfully field tested bioaugmentation for CT degradation with this organism, and have the genes involved in synthesis of the cellular component that carries out this interesting process. With the further development here proposed, we will gain an understanding of what conditions are required to produce the dehalogenating factor and how best to apply this organism or the dehalogenating factor it produces for in situ biodegradation of carbon tetrachloride. The three phases represent an integrated approach to addressing an important in situ remediation process.

## Annual Progress Report

### 2001 Progress Report

### 2002 Progress Report

# Environmental Management Science Program Research in California

## Lawrence Berkeley National Laboratory

### 70069 – Fast Flow in Unsaturated Coarse Sediments

**Principal Investigator:** Dr. Tetsu K. Tokunaga

**Problem Area:** Subsurface Contamination

This research proposal was developed to improve our understanding of the physics of unsaturated flow in coarse- to very coarse-textured sediments, and through this meet practical needs related to contaminant transport in such vadose environments. This is a critical area for improving our basic understanding of vadose zone flow and transport because it contains aspects that are beyond the realm predictable by classical Miller-Miller scaling analyses. In particular, very coarse-textured media can sustain high flow rates at low saturations, and do so via film flow rather than by flow through an interconnected network of saturated pores. Thus, the physics of fast flow processes in unsaturated very coarse media is fundamentally different from that traditionally recognized in finer textured sediments. Developing an understanding of unsaturated flow in very coarse media is also essential for pragmatic purposes including the management of severely contaminated DOE sites, the use of coarse granular media in engineering subsurface waste isolation systems, and the fact that such sediments can support very fast flow and transport. Some of the most badly contaminated sites under DOE custody are found at Hanford, Washington, where much of the vadose zone consists of gravels and gravelly sands. Without understanding the basic processes unique to fast, unsaturated flow in such coarse sediments, our abilities to predict contaminant transport in such environments will remain poor. Such understanding is also needed because layers of unsaturated coarse granular sediments are now being used for vadose zone waste isolation in engineered “capillary barriers”. Such systems work best when infiltration is low and uniformly distributed, without significant preferential flow. Deep migration of contaminants at Hanford and other sites through texturally stratified vadose zones provide “natural” analogs showing that the capillary barrier principle has severe limitations, especially when seepage originates for very localized sources such as that expected from leaking tanks. Here again, we need to better understand the physics of unsaturated flow in very coarse granular media in order to improve our ability to isolate wastes in the vadose zone.

Problems of contaminant transport in the vadose zone are very complex because of subsurface heterogeneity, waste-sediment reaction induced alteration of sediment properties, and our lack of understanding of certain basic processes even in the absence of heterogeneity and reactions. This proposal focuses on an important area in need of basic understanding; flow in unsaturated, very coarse sediments. We start by identifying problems with applying existing pore-scale conceptual models for unsaturated flow to very coarse-textured sediments, through which the importance of film flow emerges. Recent insights into the physics of film flow on unsaturated fracture surfaces are then applied to the case of film flow on gravel surfaces. These previous measurements and recent calculations indicate that fast flow can occur in very coarse-textured media, at low saturations. The proposed research is designed to further test these results through a series of macroscopic and microscopic experiments on very coarse sediments having a variety of surface roughnesses and wettabilities. The macroscopic experiments consist primarily of soil physics methods modified to obtain bulk unsaturated hydraulic properties of coarse sediments in the energy range most relevant to fast, unsaturated flow. This energy range spans matric potentials from about -10 to 0 kPa. The macroscopic measurements will provide valuable additions to the currently sparse data on unsaturated hydraulic properties of very coarse sediments. The microscopic measurement of film flow and unsaturated pore-scale hydrodynamics will provide mechanistic explanations for the observed macroscopic properties and processes. To better understand transient flow across coarse textural interfaces and also explore limitation of capillary barrier performance, experiments will also be conducted on texturally stratified systems. This set of investigations will result in a comprehensive understanding of fast flow through unsaturated coarse sediments, integrating microscale mechanisms with bulk system behavior. Progress in predicting vadose zone contaminant transport and remediation requires this understanding.

## **Annual Progress Reports**

**2000 Progress Report**

**2001 Progress Report**

# Environmental Management Science Program Research in Colorado

## University of Colorado

### 70070 – Reactivity of Primary Soil Minerals and Secondary Precipitates Beneath Leaking Hanford Waste Tanks

**Principal Investigator:** Kathryn L. Nagy

**Problem Area:** Subsurface Contamination

Since the late 1950s, leaks from 67 single-shell tanks at the Hanford Site have been detected or suspected, resulting in the release of about 1 million curies to the underlying sediments. The Hanford Tri-Party Agreement calls for the initiation of remediation at the 200 Area tank farms in 2004. There is a risk that these activities may add to and/or mobilize the existing inventory of contaminants in the vadose zone. At issue is the distribution of contaminants beneath the tanks, the processes that led to their current disposition, and the processes that will control their future mobility. The high ionic strength, high pH, and high aluminum concentrations in the tank liquids can significantly alter the vadose zone sediments through dissolution of primary minerals and precipitation of secondary minerals. These processes directly influence (1) the flow paths that control contaminant transport and (2) the reactivity of the solid matrix that controls contaminant mobility. Scientifically defensible decisions on tank remediation must consider the impact of these physical and geochemical processes. However, fundamental knowledge is lacking on the mineral reaction kinetics and the dynamic interaction of the reactions with the flow field and contaminant sorption.

The dominant reaction expected is precipitation of Al-hydrous oxides in response to mixing of tank solutions with ambient Hanford soils and solutions. However, at the extreme solution conditions found in the tanks, little is known about the phases that might form and their formation rates. Depending on the mixing conditions, stable or metastable phases might precipitate. The rates at which these reactions occur will depend on the kinetic factors of temperature, solution composition, and reactive surface area. At high supersaturations, polymeric Al-species may precipitate as colloids, and adsorb to other minerals to be transported in solution. Dissolution of primary soil minerals will provide components that can reprecipitate with Al as smectite clays, zeolites, or layered double hydroxides. Sorption and desorption of radionuclide contaminants will be a strong function of the amount of surface area of the neoformed Al-phases and may fluctuate as the amounts of these highly reactive Al-phases vary with changes in the ambient environment. Clearly, multiple reactions will occur simultaneously and compete with each other in how they alter flow paths and control contaminant migration.

We propose to address three specific issues with respect to obtaining accurate rate laws for the particular system of mixed tank fluids and Hanford soils.

*Recognized factors that control the kinetics of dissolution and precipitation must be quantified for the unnatural system of tank solutions mixing with soils, including effects of high pH, high ionic strength (especially  $\text{NaNO}_3$  solutions), temperature, and saturation state.*

*A clear understanding of the role of nucleation mechanisms of the secondary precipitates must be obtained. Understanding nucleation mechanism, nucleation sites on soils minerals, and the role of reactive surface area in simultaneous dissolution and precipitation reactions are the key unknown components in comprehending this contaminated soil system.*

*New knowledge obtained in (1) and (2) will be the basis for building a mechanistic understanding of these processes in the context of tank fluids migrating through the vadose zone. Localized changes in porosity and permeability will dictate preferential flow paths for the leaking fluids which directly regulates the transport of later arriving chemical species. Conversely, changes in mineral surface area affect the number and type of sorption sites which controls the reactivity of the solid matrix. A comprehensive model that integrates our best understanding of these feedback mechanisms with all the critically available data is necessary to test the validity of our approach.*

## **Annual Progress Report**

### **2001 Progress Report**

# Environmental Management Science Program Research in Ohio

## Ohio State University

### 70081 – Immobilization of Radionuclides in the Hanford Vadose Zone by Incorporation in Solid Phases

**Principal Investigator:** Dr. Samuel J. Traina

**Problem Area:** Subsurface Contamination

Soluble radionuclide contaminants in soils, groundwaters, and tank wastes on DOE sites can sorb to, or desorb from particle surfaces depending on a number of variables. When sorbed as surface complexes, such contaminants are susceptible to changes in solution pH and ionic strength, the effect of organic ligands and oxoanions (e.g., phosphate or carbonate), and other variables, which can cause contaminants to be desorbed and mobilized. However, incorporation of the contaminant in stable insoluble solids that don't easily exchange the contaminant ion with other solution species, can immobilize and isolate it from the biosphere. Incorporation can be accomplished in any of several ways, including absorption of the contaminant into a host solid to which it was initially adsorbed, and precipitation of a solid phase containing the contaminant. Precipitation processes can include reactions with other native or introduced solutes to form a simple solid compound of the contaminant like a hydroxide, a carbonate, or a phosphate. In a process sometimes called "neof ormation", reaction with material dissolved from a host solid can result in either recrystallization of the host phase and incorporation of the contaminant into its structure (co-precipitation), or the formation of a new solid compound containing the contaminant as well as a dissolved component of the host solid.

The leaking underground storage tanks at the DOE's Hanford Reservation pose a particularly complex geochemical problem involving the processes discussed above. The high concentrations of dissolved Al as well as the exceptionally high pH (> 13) and ionic strengths of the fluids present in many of these tanks make it probable that tank leachates will contain large concentrations of  $\text{Al}(\text{OH})_4^-$  ions. Upon reaction with the soil matrix, this will potentially result in the formation of a number of complex precipitates that could incorporate contaminant species from the tanks. Reaction of the tank fluids with the soil matrix should cause some dissolution of the soil minerals, releasing Si into solution, and decreasing pH. These solution conditions should promote the formation of Al- and Si-hydroxide gels, hydrotalcites, and ultimately Al-(hydr)oxides. The potential for zeolite formation may also be present. All of these potential phases have high surface reactivities, and should serve as strong sorbents and/or coprecipitates for contaminant ions also present in the leachate (Cs, Co, Sr, Tc, U). These chemical transformations should result in dramatic changes in the fate and transport of the contaminant ions associated with tank fluids. Clearly, more information is needed before an understanding of the complex geochemical environment in the vadose zone beneath the Hanford tanks is attained.

In this three-year collaborative, multi-institutional project, we propose to investigate (1) the effect of aging on the stability of sorption complexes of Co, Cs, Sr, Tc and U, on Al-oxide and Al-oxyhydroxide surfaces formed from neutralization and homogeneous nucleation from alkaline aluminate solutions; (2) sorption/coprecipitation of these elements in solids formed from reaction of alkaline aluminate solutions with minerals representative of the soils and sediments underlying the Hanford Tank Farm (e.g., quartz, feldspars, clays); and (3) the sorption/coprecipitation of these elements in solids formed from reaction of alkaline aluminate solutions with soil and sediment samples from the Hanford sites. (4) To couple these laboratory studies to precipitation processes occurring in the Hanford vadose zone beneath the Tank Farm, we also propose to characterize the particle coatings and precipitate phases in core samples from this zone. These investigations will utilize XAFS, NMR, and vibrational spectroscopies, electron and X-ray microprobe analyses, transmission electron microscopy, XPS, and other characterization methods sensitive to the speciation and spatial distribution of these ions in several model systems.

## **Annual Progress Reports**

**2000 Progress Report**

**2001 Progress Report**



# Environmental Management Science Program Research in New Mexico

## New Mexico Institute of Mining and Technology

### 70088 – Interfacial Reduction-Oxidation Mechanisms Governing Fate and Transport of Contaminants in the Vadose Zone

**Principal Investigator:** Dr. Baolin Deng

**Problem Area:** Subsurface Contamination

Immobilization of toxic and radioactive metals (e.g., Cr, Tc, U) in the vadose zone by In-Situ Gas Reduction (ISGR) is a promising technology being developed by Pacific Northwest National Laboratory (PNNL) for soil remediation. Earlier studies have shown that Cr(VI) in a number of soil samples can be effectively immobilized by treatment with diluted hydrogen sulfide ( $H_2S$ ). A field test has been completed that resulted in 70% immobilization of Cr(VI). In particular, the health and safety issues related to ISGR have been well resolved through the field demonstration. The residual  $H_2S$  gas can also be recovered so no secondary contamination takes place. Nevertheless, any scientific questions underlying the vadose zone treatment by  $H_2S$  are not fully understood. The detailed kinetics and mechanisms for Cr(VI) immobilization are unknown. The speciation of Cr(VI) and  $H_2S$  after the treatment has not been fully characterized. A legitimate concern with the remediation system is the longevity of immobilization after  $H_2S$  treatment is completed. Although it is likely that Cr will remain immobilized once Cr(VI) is reduced to Cr(III), the long-term stability still needs to be carefully examined by experiments. Our preliminary study shows that soil mineral surfaces may significantly affect ISGR performance by acting as catalysts in Cr(VI)- $H_2S$ -Soil systems. The mechanism of such catalysis needs to be illustrated. If the concept of ISGR can be applied to Tc and U, as well as to Cr, the technology may have a major impact on the vadose zone remediation of the contaminant metals at many DOE sites.

In order to improve the design of ISGR and evaluate its overall capability, scientific knowledge is urgently needed concerning the kinetics and mechanism of interaction among  $H_2S$ , the metal contaminants, and soil components. The proposed joint project involving New Mexico Institute of Mining and Technology and PNNL will draw complementary expertise to seek an improved understanding of the relevant processes. Substantial batch and column experiments will be performed in order to collect kinetic information. In collaboration with spectroscopic studies, a mechanistic understanding will be developed on the interfacial redox transformation. In addition, a model incorporating the reaction kinetics and  $H_2S$  gas flow will be developed, which can be used for designing an improved ISGR system. In order to make substantial progress in a three-year period, the following specific research tasks will be accomplished: (A) Evaluation of the potential catalytic effect of mineral surfaces on the rate of Cr(VI) reduction by  $H_2S$  and the rate of  $H_2S$  oxidation by air. (B) Identification of soil iron oxide reactions with  $H_2S$  and associated reaction rates and products. (C) Evaluation of the role of soil water chemistry on the reduction of Cr(VI) by  $H_2S$ . (D) Assessment of the reductive buffering capacity of  $H_2S$ -reduced soil and the potential for emplacement of long-term vadose zone reactive barriers. (E) Evaluation of the potential for immobilization of Tc and U in the vadose zone by reduction and an assessment of the potential for remobilization by subsequent reoxidation.

We believe the project will significantly enhance our capability to better characterize the fate and transport of Cr, Tc, and U in the vadose zone, to predict the long-term stability of the treatment, and to provide insights as how to improve the design and application of the ISGR remediation approach. The proposed endeavor will also enhance our conceptual understanding of metal reduction processes, especially the catalytic processes and mechanisms that have not been fully explored before but, we believe, are controlling many geochemical processes in soils.

## **Annual Progress Report**

**2001 Progress Report**

**2002 Progress Report**

# Environmental Management Science Program Research in California

## Stanford University

### 70115 – The Use of Radar Methods to Determine Moisture Content in the Vadose Zone

**Principal Investigator:** Dr. Rosemary Knight

**Problem Area:** Subsurface Contamination

Moisture content is a critical parameter affecting both liquid-phase and vapor-phase contaminant transport in the vadose zone. This means that accurate estimates of *in situ* moisture content must be obtained in order to design for the appropriate handling or remediation of a contaminated region of the vadose zone. The overall objective of our proposed research is to further develop the usefulness of radar methods (ground-based and borehole) as a means of characterizing moisture content in the vadose zone.

In our research we will focus on two specific aspects of the link between radar images and moisture content. The first aspect or question we address is: *Can we use a measure of the dielectric constant of a volume of the subsurface to determine the moisture content of that volume?* In addressing this first question, our focus is on determining the optimal way to transform a 3-D map of dielectric constants into a 3-D map of moisture content; i.e. the rock physics step. This is clearly a critical step in the use of radar information, and is a step that requires significant improvements in rock physics, as it is currently applied to such problems. Through theoretical modeling and laboratory and numerical experiments, we will first explore the errors that will result in determined moisture content if we use the standard rock physics relationships, which assume that moisture content is homogeneously distributed, for a subsurface region that is truly heterogeneous. In this part of our research we will develop a rigorous theoretical basis for predicting the uncertainty. For some applications involved with characterization of the vadose zone, it might be sufficient to determine the potential error or uncertainty in moisture content that will be introduced by use of the standard models; the uncertainty could be incorporated in models of contaminant transport. Having quantified the possible level of error, we will investigate ways in which the combined use of surface and borehole radar data can be used to reduce the error. Two specific ideas that will be investigated are determining the magnitude of anisotropy in dielectric measurements; and incorporating information about attenuation.

The second question we address is: *Can we use the spatial distribution of radar reflections as a means of characterizing the spatial distribution of moisture content in the subsurface?* This aspect of our research addresses the direct use of the radar image for quantifying the spatial heterogeneity of moisture content in the subsurface. This problem involves two separate issues. The first is the development of processing methods to improve the resolution of the radar image. This would provide a closer link between the moisture variation in the subsurface, the related dielectric variation, and the location, continuity and amplitude of reflections. The second issue is the development of improved methodologies for analyzing the radar image to quantify the observed spatial variability. We propose to investigate the use of wavelet transforms as an improved means of quantifying the scale-dependent spatial variability of the subsurface. The use of wavelet transforms is a method ideally suited to analyzing systems in which there are many scales of structure or heterogeneity, as are present in natural geologic systems. The development of this methodology for the analysis of radar images may provide a new way to quantitatively characterize, at many different scales, the spatial heterogeneity of moisture content in the subsurface.

This proposal is a combination of laboratory, field and theoretical studies and addresses a number of issues all of which are related to the improved use of radar methods to determine moisture content in the vadose zone. The close link between imaged dielectric properties and moisture content strongly suggests that this is an ideal approach to obtaining estimates of *in situ* moisture content, a critical factor in addressing issues associated with contaminant transport in the vadose zone. The successful completion of this proposed research will allow for improved accuracy in extracting information about both the magnitude of moisture content and its spatial distribution in the vadose zone.

## **Annual Progress Reports**

**2000 Progress Report**

**2001 Progress Report**

**2002 Progress Report**

# Environmental Management Science Program Research in Washington

## Pacific Northwest National Laboratory

### 70121 – The Influence of Calcium Carbonate Grain Coatings on Contaminant Reactivity in Vadose Zone Sediments

**Principal Investigator:** Dr. John M. Zachara

**Problem Area:** Subsurface Contamination

Fundamental research is proposed to investigate the role of calcium carbonate grain coatings on the vadose zone chemical reactivity of key Hanford contaminants (i.e.,  $^{60}\text{Co}^{2+}$ ,  $^{90}\text{Sr}^{2+}$ ,  $\text{CrO}_4^{2-}$ , and  $^{99}\text{TcO}_4^-$ ). Calcium carbonate is widely distributed through the Hanford vadose zone as a result of current and past geochemical processes, and exists as grain coatings and intergrain fill. It also results from the interaction of high level waste (e.g., high in  $\text{Na}^+$  and  $\text{OH}^-$ ) with Ca-saturated subsurface sediments. While secondary iron-, aluminum-, and manganese-oxyhydroxide grain coatings are known to control the sorption chemistry of non-calcareous sediments for inorganic ions, no comparable understanding exists for carbonate grain coatings, which may be equally or more abundant in certain situations. We hypothesize that carbonate coatings enhance the sorption of carbonate compatible contaminants (e.g.,  $^{90}\text{Sr}$ ,  $^{60}\text{Co}$ ) through a combination of adsorption and co-precipitation processes, but interfere with the reductive immobilization of the oxoanions  $\text{CrO}_4^{2-}$  and  $\text{TcO}_4^-$  by passivating electron dense surfaces of  $\text{Fe}^{2+}$ - minerals such as magnetite and biotite in Hanford sediments.

This project will explore the behavior of calcium carbonate grain coatings including how they form and dissolve (e.g., natural and waste fluid induced), their reactivity toward contaminants under water-saturated and unsaturated conditions, their impact on the reactivity of the mineral substrate, and their in-ground composition and minor element enrichment. The goal is to provide an improved understanding of contaminant sequestration/immobilization reactions that can be scaled to macroscopic reactive transport models used to forecast contaminant migration. Our scientific focus will be on the influence of the coatings on, 1.) surface coordination or co-precipitation reactions, and 2.) electron transfer reactions that can result in the immobilization of redox-sensitive contaminants. Modern surface- and bulk-sensitive structural and imaging methods including X-ray absorption spectroscopy, scanning probe microscopy, photoelectron spectroscopies, and others will be applied in concert with judiciously designed model systems such as epitaxially grown surfaces of known crystallographic orientation and structure to provide a rigorous molecular and microscopic understanding of the controlling reactions of target contaminant ions with carbonate-coated mineral surfaces. Model system studies will be linked with parallel spectroscopic, microscopic, and macroscopic investigations of calcareous Hanford sediments, to provide basic scientific information for the remediation/closure of Hanford and other DOE sites.

## Annual Progress Report

### 2001 Progress Report

### 2002 Progress Report

# Environmental Management Science Program Research in Pennsylvania

## Pennsylvania State University

### 70126 – Collaboration: Interfacial Soil Chemistry of Radionuclides in the Unsaturated Zone

**Principal Investigator:** Dr. Jon D. Chorover

**Problem Area:** Subsurface Contamination

Mobility of radionuclides ( $\text{Cs}^+$ ,  $\text{Sr}^{2+}$ ) in the vadose zone is controlled by sorptive interactions with natural soil particles. Weathering of silicates and intercalation of clay minerals with hydroxy -aluminum and -aluminosilicate species under the intense geochemical conditions introduced by DOE wastes, in addition to sorption of natural organic matter (NOM), alters particle surface chemistry, but effects on surface affinity for radionuclides retention are not known. The focus of this study will be on the sorption of  $\text{Cs}^+$  and  $\text{Sr}^{2+}$  onto altered clay surfaces in the presence of high levels of competing cations  $\text{Na}^+$  and  $\text{Ca}^{2+}$  (up to molar levels) and neutral to high pH (to pH 14) as often encountered at DOE waste sites. The effects of waste liquor neutralization by soil water will also be investigated. Few studies have been conducted to elucidate sorption/ion exchange of radionuclides on clays at these extreme solution conditions and at relative humidities less than saturation. To determine why surface alteration affects binding of radionuclides, detailed information on the molecular environment of sorbed contaminants is needed. The main objectives of this work, therefore, are to: I) quantify the rate and extent of radionuclide sorption/desorption on pristine and altered clay surfaces through macroscopic batch and column experiments, ii) investigate dissolution behavior of layer silicates induced by these extreme geochemical conditions using XRD, FTIR, and NMR spectroscopies, and iii) identify the mechanisms of interaction at the molecular level using NMR and X-ray absorption spectroscopies.

Expected Results: Rates of sorption/desorption and conditional selectivity ( $K_{\text{ex}}$ ) and partition ( $K_d$ ) coefficients that can be used to quantify the sorption/exchange reaction of radionuclides with minerals will be determined. These values will be obtained as a function of aqueous chemistry representing the continuum between concentrated waste liquor and dilute soil solution end-members and also for various sorbent conditions (i.e., pristine, weathered and coated clays, whole Hanford soils). Mechanisms of interactions (strength of sorption, type of sorption sites) will be elucidated at a molecular level using methods developed in our laboratories.

Approach: Macroscopic experiments will be conducted in batch and column modes. Initial experiments will involve model clays to facilitate mechanistic investigations, and then extended to Hanford soils. Distribution of radionuclides among free, aqueous-humic-bound, and mineral (illite, vermiculite, smectite, and kaolinite)-humic-bound forms in heterogeneous systems will be determined using equilibrium dialysis. The role of high-affinity sites (e.g., siloxane, frayed edge sites [FES]) in influencing radionuclide fixation with contaminant aging will be evaluated using isotopic exchange and desorption (infinite bath) techniques. Changes in the density/accessibility to FES caused by hydroxy/NOM coatings on clay surfaces will also be investigated. XRD, FTIR, and NMR analyses will permit monitoring dynamic dissolution-reprecipitation disequilibrium induced by high pH and Al conditions. NMR investigations of sorption interactions will involve the use of cross polarization (CP), rotational-echo double-resonance (REDOR), and double- and triple-resonance transfer of populations by double-resonance (TRAPDOR) techniques. These new methods will provide direct information on ion exchange dynamics and proximity in space of  $^{133}\text{Cs}$  and interacting mineral framework species. Details of the local structural environment around the sorbed radionuclide and nature of the sorption complex (e.g., inner versus outer sphere) will be obtained using X-ray absorption spectroscopy.

## **Annual Progress Report**

**2001 Progress Report**

**2002 Progress Report**

# **Environmental Management Science Program Research in Massachusetts**

## **Woods Hole Oceanographic Institution**

### **70132 – Speciation, Mobility and Fate of Actinide sin the Groundwater at the Hanford Site**

**Principal Investigator:** Dr. Ken O. Buesseler

**Problem Area:** Subsurface Contamination

We suggest that there are gaps and inconsistencies in our understanding of actinide behavior in groundwater due to the widely varying properties of Pu from different sources and due to variations in sampling and analytical methodologies. It is our intent to sample across defined contaminant plumes at the Hanford Site for Pu and other actinides. Samples are collected using a “micro-purge” low pumping rate technique and directly separated into truly dissolved and colloidal size classes with an ultra-clean cross-flow filtration (CFF) system. Pu redox samples are separated immediately in the field and ancillary samples are also carefully collected for supporting organic and basic geochemical analyses. High sensitivity thermal ionization mass spectrometry (TIMS) is used to detect the Pu isotopes in all size and redox fractions, thus providing information not only on Pu concentrations but on the Pu source, which can strongly influence Pu speciation and mobility. The combination of these state-of-the-art procedures and the demonstrated care taken to process these samples ensures that the data represent the original in-situ speciation. The results of such a careful basic research program would: i) provide the basis for accurate modeling and prediction of actinide transport; ii) allow for remediation strategies to be planned that might use in-situ manipulations of geochemical variables to enhance (for extraction) or retard (for immobilization) Pu mobility in the vadose/groundwater zone, and iii) identify specific Pu sources and the extent of far field, or long-term migration of actinides in groundwaters. This new knowledge is essential to ensure continued public and worker safety at the DOE sites and the efficient management of cleanup and containment strategies.

## **Annual Progress Report**

### **2001 Progress Report**



# Environmental Management Science Program Research in Washington

## Washington State University

### 70135 – Colloid-Facilitated Transport of Radionuclides Through the Vadose Zone

**Principal Investigator:** Dr. Markus Flury

**Problem Area:** Subsurface Contamination

Radioactive and hazardous waste stored in the underground tanks at the Hanford site has leaked or is suspected to have leaked into the vadose zone. Radionuclides, which are normally considered to be strongly sorbed (e.g., Pu and Cs), have been detected at much deeper depth than predicted based on current theories of vadose zone contaminant transport. There is strong indication that contaminants can be transported via colloids. Such colloid-facilitated transport is likely to occur at the Hanford site, where contaminants leaking from the storage tanks are released directly to the vadose zone. At Hanford, the potential for *in situ* formation of colloids as leaking tank waste enters the vadose zone is high. Tank waste supernatants are known to consist of solutions with high pH, ionic strength, and aluminate concentrations. When such alkaline solutions contact soils and sediments around the tanks, it is likely that soluble silica-rich allophane, feldspathoids, and zeolite-like materials are formed. These negatively-charged colloids are capable of adsorbing or coprecipitating with contaminant cations and moving through soil and sediment matrices. The objectives of this proposed project are to study three major processes responsible for colloid-facilitated transport: (1) formation and mobilization of colloids, (2) association of contaminants with colloidal particles, and (3) co-transport of colloids and contaminants in the vadose zone. We specifically consider chemical and geochemical conditions at the Hanford site. The radionuclide Cs is selected as a model contaminant. Soil or sediment samples representative of the porous material under waste storage tanks will be collected at the Hanford site. Formation of colloids will be studied in batch systems by reacting solutions typical for tank waste with vadose zone materials and with solutions expected at equilibrium with soil material. Colloids will be separated and characterized in terms of size, structure, composition, and surface charge characteristics. The interactions of Cs with colloidal particles isolated from the previous step will be investigated with batch sorption experiments and spectroscopic techniques. Transport and co-transport of colloids and the radionuclide Cs will then be studied with a series of laboratory column experiments using repacked Hanford sand material. Experiments will be carried out under unsaturated, steady-state as well as transient water flow to study the effect of water content on colloid transport. Magnetic Resonance Imaging will be used to visualize colloidal movement inside the porous medium. Sorption studies and column outflow data will be analyzed with numerical models to elucidate the relevant mechanisms responsible for contaminant sorption as well as colloid and radionuclide transport. Sorption and reaction models will be combined with transport models to quantitatively describe the column experiments. The results of the proposed research will lead to a better understanding of colloid-formation, colloid-contaminant-soil interactions, colloid migration, and colloid-facilitated transport in the vadose zone. The experiments proposed use conditions specific to the Hanford site, and the results are therefore directly applicable to clean-up strategies and procedures for Hanford contamination problems. We expect to provide conclusive evidence under what conditions, if any, colloid-facilitated transport can be expected at the Hanford site, and what the quantitative magnitude of this transport process will be.

## Annual Progress Report

### 2001 Progress Report

### 2002 Progress Report

# **Environmental Management Science Program Research in New York**

## **State University of New York at Stony Brook**

### **70146 – Spectroscopic and Microscopic Characterization of Contaminant Uptake and Retention by Carbonates in Soils and Vadose Zone Sediments**

**Principal Investigator:** Dr. Richard J. Reeder

**Problem Area:** Subsurface Contamination

The release and migration of toxic metals and radionuclides within the subsurface and vadose zones at various sites over the DOE Complex pose serious technological challenges for remediation. The design and implementation of cost-effective remediation strategies require knowledge of the factors that govern contaminant mobility and reactivity within their host materials. Calcium carbonate, resulting from pedogenic processes, is an important component of soils and vadose-zone materials at the Hanford Site, where it coats grains and occurs as a massive caliche layer at depth. We propose a collaborative project to characterize the uptake and retention of contaminants (Co, Cs, Pb, Sr, Cr, and U) on calcium carbonate (calcite), with a focus on conditions and materials relevant to this site. The research plan calls for detailed microscopic and spectroscopic characterization of carbonate coatings and caliche from the Hanford Site, combined with an assessment of the heterogeneity of reactive surface sites that could influence contaminant uptake properties or long-term retention. This will rely on microscopic study as well as mineralogic and geochemical characterization. Spatially resolved X-ray fluorescence and X-ray absorption spectroscopy (micro-XRF/XAS) as well as X-ray photoelectron spectroscopy (XPS) will be used to map the distribution of contaminant reaction products after exposure to natural and model carbonate substrates. These results will have direct application for assessing the reactive fraction of available surface area on carbonates from the affected site.

Adsorption and desorption experiments for target contaminants on calcite will be conducted using radioisotope and high-precision gamma-counting methods to determine both the kinetics and extents of uptake from solutions over a pH range relevant to site conditions. Desorption will test the tendency for long-term retention of contaminants on calcite. Because existing studies suggest that adsorption onto calcite results in co-precipitation, which would have a major influence on potential re-release, it is essential to determine the chemical state of the adsorbed metals, i.e., its speciation. Contaminant speciation will be determined in situ using X-ray absorption fine structure (XAFS) spectroscopy of “wet slurries” as a function of duration of adsorption and surface coverage. This element-specific technique provides information on oxidation state, molecular formula and structure, and identity of ligands, and allows distinction between inner-sphere and outer-sphere type surface complexes as well as between co-precipitation and surface precipitation. Separate co-precipitation experiments with target contaminants will allow an assessment of the effectiveness of uptake during crystallization of calcite, which is favored in the soil and vadose zone as a result of periodic wetting and drying, and also in response to the highly alkaline waste fluids. XAFS spectroscopy will again be used to confirm speciation.

The results of this comprehensive study will provide detailed information on contaminant speciation, physical and chemical properties of subsurface carbonate phases, and the reactions involving calcium carbonates that occur in the subsurface zone for a site relevant to DOE goals. These are essential components of models necessary for predicting contaminant mobility and for designing effective technologies for the recovery or immobilization of contaminants.

## **Annual Progress Report**

### **2001 Progress Report**

# **Environmental Management Science Program Research in California**

## **Lawrence Livermore National Laboratory**

### **70149 – The Dynamics of Vadose Zone Transport: A Field and Modeling Study Using the Vadose Zone Observatory**

**Principal Investigator:** Dr. Charles R. Carrigan

**Problem Area:** Subsurface Contamination

A stated need of the DOE EM program is a better understanding of basic vadose zone fluid flow and contaminant transport processes for the purpose of making improved estimates of contaminant release rates and fluxes across the vadose zone to the water table at DOE sites such as the tank farms at Hanford. We propose to investigate details of the modes of contaminant transport with the aid of infiltration experiments designed to elucidate how vadose zone characteristics such as preferential pathways, heterogeneities, and relative permeabilities influence the transport of contamination in liquid, gas and colloidal phases to the water table. Beyond enhancing our basic understanding of vadose zone transports processes, this proposed effort would result in a vadose-zone-transport-characterization methodology that can be generalized to other DOE sites. To accomplish this, we will use the newly developed Vadose Zone Observatory (VZO) at Lawrence Livermore National Laboratory (LLNL) to carry out a partially subsidized, highly cost-effective study of multiphase fluid flow and colloidal transport in a heterogeneous unsaturated zone bearing dynamic resemblance to one type of Hanford vadose regime. The observatory consists of almost twenty instrumented boreholes and monitoring wells which traverse the 70-foot unsaturated zone including eight wells containing electric resistance tomography (ERT) arrays, four wells for electromagnetic induction tomography (EIT) and water table sampling, and four boreholes with multilevel gas-sampling ports, soil temperature sensors, gypsum blocks, tensiometers and lysimeters. The observatory uses several multichannel data loggers to continuously store information about surface barometric pressure, subsurface gas-phase pressure, subsurface temperature, capillarity and water-table levels that is downloaded into computers for later analysis. Using the capabilities of the VZO, we will continuously monitor the progress of an infiltration event simultaneously using both geophysical volumetric imaging techniques as well as more conventional hydrologic measurements (e.g., subsurface temperature, gas-phase pressure, tensiometry and lysimetry) that involve making observations at discrete points throughout the infiltration volume. An advantage of this approach is that volumetric imaging provides a context for interpreting the discrete observations, while discrete measurements provide a more detailed picture of changes in the vadose zone that cannot be obtained from the volumetric imaging observations themselves. Beyond this, the VZO permits samples of moisture and gases to be taken from many different depths in the vadose zone and from the water table. This ability to sample is critical to our infiltration experiments, which include a variety of chemical and isotopic gas- and liquid-phase tracers and colloidal particles. The release of chemical and isotopic tracers during infiltration events is an important feature of these proposed experiments since such tracers permit evaluation of the potentially complicated relationship between actual chemical transport and fluid flow in the unsaturated zone as determined by ERT or other imaging methods. With the goal of providing a comprehensive picture of multiphase vadose zone flow and transport, LLNL's NUFT (Non-isothermal Unsaturated Flow and Transport) computer program will be used to develop diagnostic models that serve as a framework for interpreting the wide variety of observations obtained during an infiltration experiment. With support from a hydrogeologist at Hanford, modeling will also provide the basis for applying our enhanced understanding of contaminant transport at the VZO to addressing transport issues at Hanford. Finally, by carrying out some infiltration experiments jointly with other LLNL principal investigators and a geophysical instrumentation company, we will leverage our effort as well as collaborate with them in developing improved subsurface imaging interpretations and technologies based upon the ERT and electromagnetic induction methods.. In support of DOE educational programs, this proposal involves the participation of an MS-level student intern as well as a postdoctoral researcher.

## **Annual Progress Reports**

**2000 Progress Report**

**2001 Progress Report**

# Environmental Management Science Program Research in Washington

## Pacific Northwest National Laboratory

### 70163 – The Aqueous Thermodynamics and Complexation Reactions of Anionic Silica Species to High Concentration: Effects on Neutralization of Leaked Tank Wastes and Migration of Radionuclides in the Subsurface

**Principal Investigator:** Dr. Andrew R. Felmy

**Problem Area:** Subsurface Contamination

Highly basic tank wastes contain several important radionuclides, including  $^{90}\text{Sr}$ ,  $^{99}\text{Tc}$ , and  $^{60}\text{Co}$ , as well as actinide elements (isotopes of U, Pu and Am). These highly basic tank wastes are known to have leaked into the vadose zone at the Hanford Site. Upon entering the sediments in the vadose zone, such highly basic solutions dissolve large concentrations of silica from the silica and aluminosilicate minerals present in the subsurface. These dissolution reactions alter the chemical composition of the leaking solutions, transforming them from a highly basic (as high 2M NaOH) solution into a pore solution with very high dissolved silica and significantly reduced pH. This moderately basic (pH 9 to 11), high-silica solution has the potential to complex radionuclides and migrate through the subsurface. Such strong radionuclide complexation is a currently unrecognized transport vector that has the potential to expedite radionuclide transport through the vadose zone. These strong complexation effects have the ability to significantly alter current conceptual models of contaminant migration beneath leaking tanks.

Unfortunately, the necessary thermodynamic data are not available to accurately predict radionuclide complexation and transport for solutions having high dissolved silica concentrations, where silica species are highly polymerized. The equilibrium constants for monomeric radionuclide-silica complexes involving  $\text{H}_3\text{SiO}_4^-$  are comparable to those for carbonate, which is usually considered to be the principal ligand responsible for complexation and mobility of many radionuclides in groundwater systems. Radionuclide complexation by other silicate anions, the equilibrium constants for which are completely unknown, are expected to be orders of magnitude greater, based upon electrostatic charge and concentration effects alone. This situation is particularly unfortunate, given that experimental studies with Hanford sediments contacted with basic solutions have shown dissolved silica to be the principal ligand present in solution. Without knowledge of the complexation (speciation) effects of the dominant complexing ligand, there seems to be little hope that the mechanisms of radionuclide attenuation or migration in areas of the vadose zone affected by leaking tank waste ever will be unraveled. To develop such an understanding, the effects of the dominant complexing ligand must be known. The objective of this study is to develop just such a capability.

In this project, we will determine the aqueous thermodynamics and speciation of dissolved silica and silica-radionuclide complexes to high silica concentration using a combination of 1) studies of chemical species structure and composition (via nuclear magnetic resonance and, where applicable, laser-induced fluorescence spectroscopy and x-ray absorption spectroscopy); 2) molecular simulations to help identify key species structures and assist in interpreting experimental measurements; and 3) fundamental physical chemistry measurements, including solubility, electromotive force, and isopiestic measurements, to obtain the necessary thermodynamic data for predicting contaminant complexation and waste neutralization reactions. The radioactive elements we plan to study include Sr, Co, Am(III), U(VI), Tc(IV) and Th(IV) (as an analog to the tetravalent actinides).

To accomplish these tasks, we have assembled a multidisciplinary team of investigators with extensive experience and well-established expertise in aqueous thermodynamics, actinide chemistry, analytical methods and techniques and molecular modeling.

## **Annual Progress Report**

**2001 Progress Report**

**2002 Progress Report**

# **Environmental Management Science Program Research in Washington**

## **Pacific Northwest National Laboratory**

### **70165 – Integrated Field, Laboratory, and Modeling Studies to Determine the Effects of Linked Microbial and Physical Spatial Heterogeneity on Engineered Vadose Zone Bioremediation**

**Principal Investigator:** Dr. Fred J. Brockman

**Problem Area:** Subsurface Contamination

In situ bioremediation of contaminants can offer advantages in cost, speed, public acceptance, and final cleanup levels achieved relative to physical removal methods. However, the lack of knowledge on how physical and hydrologic features of the vadose zone control the spatial distribution of microbial biotransformation activity and the potential for microorganisms to colonize this region raises questions about the feasibility of deep vadose zone bioremediation, and causes very large uncertainties in the accuracy of current model predictions. The goal of this research is to provide DOE with an increased understanding of the effect of interacting hydrologic and microbiological processes which control the feasibility of engineered bioremediation of chlorinated compounds in heterogeneous, microbially sparse deep vadose zones. The specific objectives are to: (1) Evaluate an approach for removal of carbon tetrachloride from the vadose zone using enhanced biodegradation via gas-phase nutrient injection, (2) Conduct laboratory research on vadose zone microbial colonization processes - a major factor which controls the rate and extent of biotransformation in the deep vadose zone - and use the information to develop an improved vadose zone reactive transport model, and (3) Develop guidelines on the level of site characterization information that is needed for accurate premodeling of attenuation of vadose zone contaminant transport by engineered bioremediation.

## **Annual Progress Report**

[\*\*2001 Progress Report\*\*](#)

[\*\*2002 Progress Report\*\*](#)

# **Environmental Management Science Program Research in California**

## **Lawrence Berkeley National Laboratory**

### **70176 – Transuranic Interfacial Reaction Studies on Manganese Oxide Hydroxide Mineral Surfaces**

**Principal Investigator:** Dr. Heino Nitsche

**Problem Area:** Subsurface Contamination

Several DOE sites have been contaminated by transuranic radionuclide (TRU) discharges. Of these TRU, neptunium and plutonium are highly toxic and potentially mobile in the vadose zone. Modeling predictions of their potential hazard to humans require reliable estimates of migration rates. Manganese oxide/hydroxide minerals, present as minor phases, can preferentially sequester TRU over iron oxide/hydroxide minerals. The interactions between TRU and manganese oxyhydroxide minerals that determine the retardation, immobilization, and mobilization in the vadose zone are poorly understood.

Fundamental knowledge on the interfacial reactions of neptunium and plutonium with manganese oxide and hydroxide mineral surfaces relevant to contaminant transport in the vadose zone will be provided. Key thermodynamic and kinetic parameters governing the sorption of aqueous neptunium and plutonium species in defined oxidation states on characterized mineral surfaces as a function of pH, actinide concentration, and ionic strength will be determined on six manganese oxyhydroxide minerals. The influence of ethylenediaminetetraacetic acid (EDTA), microorganisms, and iron oxide/hydroxide minerals on sorption will also be determined for one site-specific manganese system. Surface complexation models will be developed to provide prerequisite information for reactive transport modeling that will lead to an improved basis for predicting TRU migration in the vadose zone to nearby water supplies.

## **Annual Progress Report**

### **2001 Progress Report**



# **Environmental Management Science Program Research in Washington**

## **Pacific Northwest National Laboratory**

### **70177 – Technetium Attenuation in the Vadose Zone: Role of Mineral Interactions**

**Principal Investigator:** Dr. Nancy J. Hess

**Problem Area:** Subsurface Contamination

Approximately  $4.5 \times 10^8$  L of liquid waste containing 930 Ci of  $^{99}\text{Tc}$  from uranium recovery processing were discharged directly to the ground at the Hanford Site from 1953 to 1958. As a result, the entire soil column beneath many of the disposal sites became saturated. Technetium is anticipated to be highly mobile and to readily migrate to groundwater. However, mass balance calculations indicate that more than 80% of the  $^{99}\text{Tc}$  released to the subsurface environment at Hanford may not have entered the groundwater. It is hypothesized that Tc reduction through surface-mediated reactions with  $\text{Fe}^{\text{II}}$ -containing minerals may have resulted in precipitation of low solubility TC solids, effectively immobilizing TC in the vadose zone and accounting for this discrepancy.

Published sorption studies demonstrate that limited adsorption of  $\text{Tc}^{\text{VII}}$  on  $\text{Fe}^{\text{II}}$  minerals occurs under oxic conditions. The immobilization of Tc under oxic conditions requires surface-mediated reduction of  $\text{Tc}^{\text{VII}}$  to low solubility  $\text{Tc}^{\text{IV}}$  species that precipitate. Thermodynamic data for the  $\text{Tc}^{\text{IV}}$  species and solubility limiting solids under these conditions are not available. Lack of fundamental data on these aspects seriously impairs the validity of risk assessment and the efficiency of remediation efforts.

The proposed research will determine the mechanisms of surface-mediated reduction/precipitation reactions of Tc on  $\text{Fe}^{\text{II}}$ -containing mineral surfaces, the composition of these precipitates, and build a thermodynamic database for the solubility-limiting phases and aqueous species. These results can be directly utilized in contaminant transport modeling in the vadose zone and for the design of appropriate remedial strategies for Tc.

### **Annual Progress Report**

[2001 Progress Report](#)

[2002 Progress Report](#)

# **Environmental Management Science Program Research in Washington**

## **Pacific Northwest National Laboratory**

### **70179 – Radionuclide Sensors for Water Monitoring**

**Principal Investigator:** Dr. Jay W. Grate

**Problem Area:** Subsurface Contamination

We propose a research program directed toward developing novel sensor concepts and materials for sensitive and selective determination of beta- and alpha-emitting radionuclide contaminants in water. In order to meet the requirements for isotope specific detection at ultra-low regulatory levels the proposed sensors are based on radiometric detection. In order to address the fundamental challenge of short ranges of beta and alpha particles in water, our overall approach is based on localization of preconcentration/separation chemistries directly on or within the active area of a radioactivity detector, using automated microfluidics for sample manipulation and sensor regeneration or renewal. Radionuclides of primary interest for DOE needs are Sr-90, Tc-99, and actinides.

The outcome of these investigations will be the knowledge necessary to choose appropriate chemistries for preconcentration of radionuclides with selectivity over other matrix components and interferences, new materials that combine chemical selectivity with scintillating properties, new materials that add chemical selectivity to solid state diode detectors, new preconcentrating column sensors, and improved instrumentation and signal processing for selective radionuclide sensors. New knowledge of the performance of sensing materials, sensor configurations, microfluidic techniques, and quantitative analytical approaches will provide the basis for designing effective probes and instrumentation for field analytical chemistry.

## **Annual Progress Report**

### **2001 Progress Report**

### **2002 Progress Report**

# **Environmental Management Science Program Research in Washington**

## **Pacific Northwest National Laboratory**

### **70187 – Quantifying Vadose Zone Flow and Transport Uncertainties Using a Unified, Hierarchical Approach**

**Principal Investigator:** Dr. Philip D. Meyer

**Problem Area:** Subsurface Contamination

Two of the primary factors complicating DOE's need to address vadose zone contamination are the natural heterogeneity or spatial variability of soils and sediments, and the difficulty of characterizing this variability at a sufficiently small scale. Much of the uncertainty in predicting field-scale water flow and contaminant transport behavior in the vadose zone can be attributed to these factors. Predictive models must often have a resolution of a meter or less to correctly simulate such influential processes as enhanced lateral spreading and preferential flow. For field-scale problems, however, it is generally impractical for parameterization of a model on the scale of a meter or less to rely on exhaustive measurement of soil physical and hydraulic properties. What is required instead is a general method for effectively combining small-scale direct measurements that cover a limited spatial extent, indirect measurement of soil properties at a much larger scale, and inference of soil properties to unsampled locations. The practical application of a method using this hierarchy of data types and measurement scales has not yet been demonstrated at the field scale.

This project will develop and demonstrate a general approach for modeling flow and transport in the heterogeneous vadose zone. Following a method recently presented by Rockhold et al. [1996], the approach will use geostatistical analysis, similar media scaling, and conditional simulation to estimate soil hydraulic parameters at unsampled locations from field-measured water content data and a set of scale-mean hydraulic parameters. The method of Rockhold et al. [1996] was applied very successfully to the simulation of a controlled field experiment. However, the relatively small scale of this experiment (12 m square by 6 m deep) and the abundant and detailed site characterization data do not represent the remediation and waste management problems facing DOE.

We hypothesize that the practical utility of the method of Rockhold et al. [1996] can be enhanced by making use of recent developments in methods to estimate soil hydraulic parameters from soil physical properties and in the estimation of soil water content using geophysical techniques. Our objectives are to 1) investigate the application of indirect measurements of soil properties to the method of Rockhold et al.; 2) determine the relationships between the type of data, the quantity of data, the scale of measurement, and the uncertainty in predictions of flow and transport using this method; and 3) develop guidance for the effective application of the method at field scales common to DOE vadose zone contamination problems. We will utilize data from a recent large-scale (50 m square by 15 m deep) experiment conducted at the Maricopa Agricultural Center in Arizona. Detailed soil characterization, water content, soil water tension, and electrical resistivity measurements have been collected for two controlled infiltration experiments. We will also revisit an infiltration experiment (16 m square by 20 m deep) conducted at the Hanford Site. Soil characterization data will be collected at this site to supplement the available information.

The results of the proposed research will provide a framework for guiding future vadose zone characterization activities at DOE sites, and an accurate, systematic approach for parameterizing models used for evaluating remediation alternatives and predicting contaminant transport and fate. The proposed research directly addresses issues of site characterization, uncertainty in vadose zone flow and transport simulations, and model validation. In addition, this research represents an innovative, low-cost approach for addressing key issues related to DOE's mission to remediate contaminated sites.

## **Annual Progress Report**

**2001 Progress Report**

**2002 Progress Report**

# **Environmental Management Science Program Research in Washington**

## **Pacific Northwest National Laboratory**

### **70193 – Influence of Clastic Dikes on Vertical Migration of Contaminants in the Vadose Zone at Hanford**

**Principal Investigator:** Dr. Christopher J. Murray

**Problem Area:** Subsurface Contamination

This research will test the hypothesis that clastic dikes at the Hanford Site provide preferential pathways that enhance the vertical movement of moisture and contaminants through the vadose zone. Studies indicate that contaminants have migrated to greater depths at the Hanford Site than expected. This includes the possible migration of cesium in the SX Tank Farm, and the presence of Technetium, carbon tetrachloride, and other mobile contaminants in groundwater beneath the 200 Area Tank Farms. Clastic dikes occur at many locations in both the 200 West and 200 East areas and have been proposed as potential pathways for vertical transport that could explain this deep migration of contaminants. However, reliable data on the dikes are scarce. Current flow and transport models of the vadose zone at the 200 Areas, including the Tank Farms, are based on relatively simple hydrogeologic models that assume horizontally layered sediments, with no preferential vertical flow paths. Given the uncertainty with regard to the properties of clastic dikes, an integrated study is needed to assess their geometry and internal properties, and their potential effect on vertical transport. To address those scientific needs, our proposed research includes field and modeling studies on the spatial distribution of clastic dikes, the hydrologic properties within dikes, and the potential effect of clastic injection dikes on fluid flow through the vadose zone. This research, which will be conducted at an uncontaminated site adjacent to the S-SX Tank Farm, will determine if clastic injection dikes provide fast paths for vertical transport through the vadose zone at Hanford. The study will provide models for the geometric pattern and properties of clastic dikes in the S-SX Tank Farm, which should also be suitable for other nearby Tank Farms in the 200 West Area. The scientific methodology developed in this study could also be applied to develop suitable models for other Hanford areas, such as Tank Farms in the 200 East Area, and may be applicable to modeling the effect of faults on vertical transport through sediments at other DOE sites.

## **Annual Progress Report**

[\*\*2001 Progress Report\*\*](#)

[\*\*2002 Progress Report\*\*](#)

# **Environmental Management Science Program Research in Idaho**

## **Idaho National Engineering and Environmental Laboratory**

### **70206 – Calcite Precipitation and Trace Metal Partitioning in Groundwater and the Vadose Zone: Remediation of Strontium-90 and Other Divalent Metals and Radionuclides in Arid Western Environments**

**Principal Investigator:** Robert W. Smith

**Problem Area:** Subsurface Contamination

Radionuclide and metal contaminants are present in the vadose zone and groundwater throughout the U.S. Department of Energy (DOE) weapons complex. Demonstrating in situ immobilization of these contaminants in vadose zones or groundwater plumes is a cost-effective remediation strategy. However, the implementation of in situ remediation requires definition of the mechanism that controls sequestration of the contaminants. One such mechanism for metals and radionuclides is co-precipitation of these elements in authigenic calcite and calcite overgrowths. Calcite, a common mineral in many aquifers and vadose zones in the arid western U.S., can incorporate divalent metals such as strontium, cadmium, lead, and cobalt into its crystal structures for the formation of solid solutions. The rate at which trace metals are incorporated into calcite is a function of calcite precipitation kinetics, adsorption interactions between the calcite surface and the trace metal in solution, solid solution properties of the trace metal in calcite, and also the surfaces upon which the calcite is precipitating. A fundamental understanding of the coupling of calcite precipitation and trace metal partitioning and how this may occur in aquifers and vadose environments is lacking.

The objectives of this research are to: (a) elucidate the mechanisms and rates of microbially-facilitated calcite precipitation and divalent cation adsorption/co-precipitation occurring in a natural aquifer and vadose zone perched water body as a result of the introduction of urea and (b) assess the effects of spatial variability in aquifer host rock and the associated hydro/biogeochemical processes on calcite precipitation rates and mineral phases within an aquifer.

These research objectives will be accomplished by conducting integrated laboratory and field research using sites which include a groundwater site at the Test Area North (TAN) and a perched water vadose zone site at Idaho Nuclear Technology and Engineering Center (INTEC), both located at the Idaho National Engineering and Environmental Laboratory (INEEL). The experimental focus will be on the in situ microbially-catalyzed hydrolysis of urea, which results in an increase in pH, and precipitation of calcite. The parameters for the field experiments will be developed in laboratory microcosm systems with known urea-hydrolyzing microorganisms in order to evaluate the relative importance of environmental factors (e.g., pH, metals, urea concentration, microbial presence) on the precipitation of calcite and the sequestration of metals. Field studies will couple a nutrient diffuser technology containing urea and an electron donor with a high-resolution multi-level passive groundwater sampler to conduct in situ calcite precipitation experiments in the aquifer at TAN and later in the perched water vadose zone. Through in situ incubation, we expect to determine differences in the rates of calcite precipitation as a function of vertical heterogeneity in the basalt aquifer and the presence of urea in the diffusers. These experiments will involve the formation of calcite overgrowths onto mineral templates. The mass of the overgrowths as well as the trace metal concentrations and carbon and strontium isotopic composition will be determined using thermal ionization mass spectrometry (TIMS), secondary ion mass spectrometry (SIMS), and inductively coupled plasma-mass spectrometry (ICP-MS). By using different concentrations of urea in the diffusers and by incubating the device across strata that vary markedly in permeability, we anticipate results that will allow not only a determination of feasibility of the technology in such an aquifer but also an assessment of the hydrogeological conditions that are best suited for the manipulation of geochemical conditions to promote calcite precipitation. Using traditional culture-based microbiology as well as molecular methods, we will also determine a microbiological community correlate of the calcite precipitation in the different geological strata as a means of verifying that urea-hydrolyzing microorganisms are responsible for the observed precipitation of calcite.

## **Annual Progress Report**

### **2001 Progress Report**

# **Environmental Management Science Program Research in Tennessee**

## **Oak Ridge National Laboratory**

### **70219 – Fate and Transport of Radionuclides Beneath the Hanford Tank-Farms: Unraveling Coupled Geochemical and Hydrological processes in the Vadose Zone**

**Principal Investigator:** Dr. Philip M. Jardine

**Problem Area:** Subsurface Contamination

The overall goal of this research is to provide an improved understanding and predictive capability of coupled hydrological and geochemical mechanisms that are responsible for the accelerated migration of radionuclides in the vadose zone beneath the Hanford Tank Farms. The study is motivated by the technological and scientific needs associated with the long-term management of the enormous in-ground inventories of multiple contaminants at the Hanford site. Our objectives are to (1) provide an improved understanding of how lithological discontinuities within the sediments influence the propensity for preferential flow and matrix diffusion at different water contents, (2) quantify the significance of downward vertical advection, lateral spreading, and physical nonequilibrium processes on radionuclide transport under variable hydrologic conditions, and (3) quantify the rates and mechanisms of  $^{137}\text{Cs}$ ,  $^{235/238}\text{U}$ , and  $^{99}\text{Tc}$  interaction with the solid phase under various hydrodynamic conditions and to determine how physical heterogeneities (i.e. stratification, pore regime connectivity) influence the retardation and degree of geochemical nonequilibrium during contaminant transport. The proposed work consists of two multidisciplinary tasks that seek to resolve four scientifically-rigorous hypotheses concerned with coupled hydrological and geochemical processes controlling contaminant migration in the vadose zone. Our approach involves (1) field-relevant, long-term unsaturated flow and transport experiments in undisturbed Hanford sediments, (2) multiple tracer strategies for quantifying preferential flow and nonequilibrium mass transfer processes at various water contents, and (3) a variety of novel surface analyses techniques (x-ray computed tomography, x-ray absorption spectroscopy, hyperquenching fluorescence) to quantify the distribution and chemical environment of contaminants as a function of sediment lithology and water content. The experimental and numerical results from this research will provide knowledge and information in previously unexplored areas of vadose zone fate and transport to support EM's performance/risk assessment and decision-making process for Tank Farm restoration. By unraveling fundamental contaminant transport mechanisms in complex porous media, we will provide an improved conceptual understanding and predictive capability of a variety of vadose issues within the DOE system. Further, this proposal combines DOE's commitment to environmental restoration with its commitment to major user facilities (Stanford Synchrotron Radiation Laboratory, Advanced Photon Source, Environmental Molecular Sciences Laboratory) and academic education.

## **Annual Progress Report**

### **2001 Progress Report**



# **Environmental Management Science Program Research in New Mexico**

## **Sandia National Laboratories – New Mexico**

### **70220 – High Frequency Electromagnetic Impedance Imaging for Vadose Zone and Groundwater Characterization**

**Principal Investigator:** Dr. Gregory A. Newman

**Problem Area:** Subsurface Contamination

Accurate description of transport pathways on the gross scale, the location of contamination, and characterization of heterogeneity within the vadose zone, are now realized as vital for proper treatment, confinement and stabilization of subsurface contamination at DOE waste sites. Electromagnetic (EM) methods are ideal for these tasks since they are directly sensitive to the amount of fluid present within porous media, as well as the fluid composition. At many DOE sites it is necessary to employ lower frequency (<1 MHz) or diffusive electromagnetic fields because of the inability of ground penetrating radar (GPR) to penetrate to sufficient depths. The high frequency electromagnetic impedance method, which operates in the diffusive frequency range (10 Hz to 1 MHz), as well as the low end of the spectrum employed by GPR (1 MHz - 10 MHz), is an ideal technique to delineate and map the aforementioned targets. The method has clearly shown potential to provide needed information on variations in subsurface saturation due to leaking storage tanks and perched water zones, as well as mapping geological structures related to the subsurface hydrological properties and heterogeneity within the vadose zone.

Although it exhibits certain advantages over other EM methods, the impedance method comes with a set of assumptions and practices that can limit its potential. The first is the desire to locate receivers in the far-field of the transmitter which allows the use of magnetotelluric (MT) inversion codes to interpret the data. Unfortunately, one does not precisely know when one is in the far-field of the transmitter, because this depends on the geology we desire to image. The second limiting factor is the scarcity of complete 2D and 3D inversion schemes necessary to properly invert the data. While approximate 2D schemes are now emerging, rigorous 2D and 3D inversion codes are needed to bound the range of applicability of the approximate methods. We propose to address these problems in the following manner: (1) implement full non-linear 2D/3D inverse solutions that incorporate source coordinates and polarization characteristics, (2) use these solutions to study improvements in image resolution that can be obtained by making measurements in the near and mid field regimes using multiple source fields, (3) collect data at the Hanford Reservation with recently developed earth impedance measurement systems, and (4) interpret the field data with the newly developed inversion capability as well as with additional and independent information such as well logs from boreholes. The benefit of this research to the DOE would be a combined measurement/interpretation package for non-invasive, high resolution characterization of larger transport pathways, certain types of contamination, and heterogeneity within the vadose zone at the Hanford Reservation as well as other DOE facilities.

## **Annual Progress Report**

### **2001 Progress Report**

### **2002 Progress Report**

# **Environmental Management Science Program Research in Wisconsin**

## **University of Wisconsin - Madison**

### **70267 – A Hydrologic-Geophysical Method for Characterizing Flow and Transport Processes within the Vadose Zone**

**Principal Investigator:** David Alumbaugh

**Problem Area:** Subsurface Contamination

Predictive models have often been employed to estimate fluid flow and contaminant transport rates within the vadose zone, that lies beneath many DOE hazardous waste sites. Unfortunately, these schemes have often failed to provide accurate results and have underestimated transport rates. Reasons for these inaccuracies include; 1) oversimplification of the earth model; 2) a misunderstanding of how formation heterogeneity at different scales affects flow and transport; 3) problems associated with the measurement of hydraulic properties and upscaling these measurements to the model scale; 4) a lack of understanding how man made structures such as unsealed wells and leaking tank farms affect flow and transport. **We** propose a mid-scale hydrologic test to analyze flow and transport within the vadose zone. This test will employ state of the art numerical and experimental tools that have, and are continuing to be developed under a previously funded EMSP proposal. The benefits to the DOE of this work include much better conceptual models of flow and transport mechanisms within natural heterogeneous and disturbed vadose zone deposits; a data base to compare predictive and performance assessment models describing unsaturated flow and transport; improvements on, and validations of, current state of the art hydrologic modeling schemes, and a validated experimental method that could be applied to other DOE sites to determine site specific flow and transport rates. The team of scientists from Sandia National Laboratories, the University of Arizona, the University of Wisconsin-Madison, and SteamTech Environmental Services brings a unique perspective to the project combining expertise in vadose-zone hydrology as well as inverse theory and geophysical imaging.

The proposed experiment will be conducted at the Sandia/Tech Vadose Zone (STVZ) facility where an infiltration experiment is currently being conducted to characterize flow in unsaturated media. Subsurface hydrologic conditions are being monitored using hydrological sensors as well as the electrical resistivity tomography (ERT) and cross borehole ground penetrating radar (XBGPR) geophysical methods. As deployed these two methods are complimentary in that the ERT produces full 3D estimates of subsurface properties, while the XBGPR yields only 2D images but at a higher resolution than the ERT such that finer scale processes and heterogeneities can be detected and examined. Once this infiltration has reached steady state, a hybrid hydrologic/geophysical inverse technique (HHGIT) will be employed to produce 3D estimates of hydrologic parameter distribution at the site, as well as the error associated with those estimates. A state of the art numerical transport scheme will then be employed to simulate and design transport experiments where a saline fluid is allowed to infiltrate into the subsurface at the STVZ site. The progress of field experiments will be monitored using the two geophysical methods. The resulting geophysical images will yield valuable information about transport processes within the vadose zone and the effect of disturbances such as unsealed wells on transport and flow in unsaturated conditions, and will provide a validation of both the numerical schemes employed here as well as other hydrologic modeling codes.

## **Annual Progress Reports**

### **2000 Progress Report**

### **2001 Progress Report**

## **Environmental Management Science Program Research in Kansas**

### **The University of Kansas**

#### **73731 – Automating Shallow Seismic Imaging**

**Principal Investigator:** Dr. Don W. Steeples

**Problem Area:** Subsurface Contamination

The research we are proposing as a continuation of our EMSP contribution is designed to develop ultrashallow seismic imaging into a cost-effective method that could be applicable to DOE facilities. The objective of the research proposed here is to develop and demonstrate the use of a cost-effective automated method of conducting shallow seismic surveys. We emphasize that this approach represents a significant departure from conventional seismic-survey field procedures. Our initial testing suggests that large numbers of geophones can be placed automatically by a mechanical device, which could make the application of shallow seismic reflection (SSR) considerably faster and cheaper. The imaging results obtained using the proposed automated seismic methods will be compared with results obtained using classical seismic techniques as well as GPR surveys, and, in the third year of the proposed research, demonstration surveys at one or more DOE facilities will be performed. The techniques proposed here are not limited to shallow seismic reflection methods but would also be capable of collecting data for seismic-refraction and possibly for surface-wave studies. Although the research we propose falls primarily into the field of seismology, some ground penetrating radar (GPR) data will be collected at a very small additional incremental cost for comparison and quality-control purposes.

### **Annual Progress Reports**

#### **[2002 Progress Report](#)**

# **Environmental Management Science Program Research in Michigan**

## **University of Michigan**

### **73732 – Migration and Entrapment of DNAPLs in Heterogeneous Systems: Impact of Waste and Porous Medium Composition**

**Principal Investigator:** Dr. Linda M. Abriola

**Problem Area:** Subsurface Contamination

The improper storage and disposal of hazardous dense nonaqueous phase liquids (DNAPLs) at DOE facilities have resulted in the widespread contamination of the subsurface environment. The vast majority of research concerning the flow and transport of DNAPLs has been conducted with “idealized” soils and fluids. Hence, numerical models are also typically developed for simplified conditions such as pristine (pure fluids) interfacial tensions and perfectly water-wet porous media. Previously funded EMSP research by the PI’s has been directed towards the quantification of DNAPL migration and entrapment behavior in physically and chemically heterogeneous systems. This research has demonstrated that chemical heterogeneities can have a significant influence on DNAPL fate and persistence, but has been limited to pure DNAPLs, and well defined aqueous and solid surface chemistries. In reality, many of the wastes reported at DOE sites are complex mixtures. For example, DNAPLs and surface-active compounds such as organic acids and bases were frequently disposed of together. Subsurface chemical heterogeneities may also occur at many DOE sites as a result of spatial and temporal variations in aqueous, DNAPL, and solid surface chemistries. Large errors may therefore be introduced into numerical simulations of DNAPL migration and remediation when models are based upon inaccurate simplifying assumptions. The research proposed herein seeks to bridge the gap in knowledge between these well defined systems and the complex contaminant mixtures and soils found at DOE sites. To this end, a research plan has been designed to explore the influence of DOE waste and site porous medium composition on DNAPL migration and entrapment. This research goal will be approached through a combination of laboratory and numerical experiments. Interfacial and hydraulic properties for representative DNAPL wastes and soils encompassing conditions typical of DOE sites will be measured. Results from these benchmark studies will be used to deduce mechanisms controlling system properties, and to develop regression relations and predictive procedures for their estimation. The predictive ability of such procedures will then be assessed through independent comparison between predictions and measured relations for actual DOE field soils and wastes. Experimental studies will be used to develop and refine theory and conceptual models for DNAPL fate which will be incorporated into an existing two dimensional multiphase flow and transport simulator. One- and two-dimensional DNAPL infiltration experiments will be conducted for a subset of these model wastes and soils. Comparison between infiltration data and simulator results will then be used to further assess and refine the constitutive models for interfacial and hydraulic properties, to investigate the up-scaling of findings from batch and soil column experiments to two-dimensional systems, and to experimentally validate the simulator. The refined simulator will be used to numerically explore the influence of waste and porous medium composition on DNAPL fate in more heterogeneous systems and at larger scales. The accomplishment of the research proposed herein will improve our ability to quantify interfacial and hydraulic properties, and residual saturations for complex DOE wastes and soils. Furthermore, the accuracy and flexibility of numerical models will be enhanced by incorporation of constitutive models which account for spatially and temporally varying interfacial and hydraulic properties. Ultimately, this information will aid in the characterization of DNAPL waste sources and fate, improve the estimation of remediation costs, and facilitate the selection of efficient remediation strategies.

## **Annual Progress Report**

### **2001 Progress Report**

# Environmental Management Science Program Research in Ohio

## Ohio State University

### 73745 – Permanganate Treatment of DNAPLs in Reactive Barriers and Source Zone Flooding Schemes

**Principal Investigator:** Dr. Frank W. Schwartz

**Problem Area:** Subsurface Contamination

There is considerable interest in using potassium permanganate ( $\text{KMnO}_4$ ) for the *in-situ* destruction of chlorinated ethylenes like TCE and PCE that occur in DNAPL source zones. The work of our group and others has shown that  $\text{KMnO}_4$  is capable of oxidizing various chlorinated solvents quickly and efficiently without the formation of hazardous intermediates. As the following overall reaction shows, a chlorinated solvent (here TCE) reacts with permanganate ( $\text{MnO}_4^-$ ) and forms manganese dioxide ( $\text{MnO}_2(\text{s})$ ), carbon dioxide, and chloride ion:



Several field demonstrations (e.g., Schnarr et al., 1998; West et al., 1997) show that  $\text{MnO}_4^-$  is capable of rapidly destroying chlorinated solvents. In Florida and California, there are industrial applications of the scheme to large and small sites.

In spite of apparently quite positive results, problems remain. Our studies and one at Battelle (PNL) have shown that the typical approach for delivering  $\text{KMnO}_4$  using injection and withdrawal wells to circulate many pore volumes of a  $\text{KMnO}_4$  solution through a zone of DNAPL contamination - may not likely achieve the expected, high destruction rates. The main problems are that the combination of natural medium heterogeneity and formation plugging due to the formation of  $\text{MnO}_2$  commonly diverts flow around the zones of highest contamination. The  $\text{KMnO}_4$  solution ends up being circulated without contacting the zones of greatest contamination. This problem is essential one of delivery - well systems might not be capable of effectively getting the  $\text{KMnO}_4$  to the zones of significant NAPL saturation.

We are proposing here to conduct basic research on a new delivery scheme that involves mixing the appropriate quantity of  $\text{KMnO}_4$  as a solid into the zone of DNAPL contamination. This scheme actually takes advantage of the tendency for reaction products to reduce the permeability of the treatment zone, which will control the dissolution of the solid and keep the  $\text{MnO}_4^-$  in contact with the DNAPL. What needs to be determined, however, is how various solid forms of  $\text{KMnO}_4$  behave in porous media and dissolve under the combined influence of fluid flow and  $\text{MnO}_2$  precipitation. The proposed study is a logical extension of the previously supported DOE study into the application of  $\text{MnO}_4^-$  for the *in-situ* destruction of chlorinated ethylenes.

The goals of this study are to (1) to elucidate the dissolution/reaction processes accompanying the amendment of media containing chlorinated solvents with  $\text{KMnO}_4$  and (2) to assess the potential for solid  $\text{KMnO}_4$  amendments as a scheme to clean up source zones. This proposal outlines a combined experimental/modeling study that builds on our previous DOE-sponsored work in understanding of how  $\text{KMnO}_4$  can be used with in situ clean ups of contaminated sites. The specific objectives of this study are (1) to describe through column experiments how solid forms of potassium permanganate ( $\text{KMnO}_4$ ) behave in saturated media with and without TCE and PCE. (2) to undertake flow tank studies that examine the hydraulic impact of reaction products (especially  $\text{MnO}_2$ ) on the flux of water through the zone of contamination, and (3) to represent the process understanding in flow and transport models that demonstrate the potential applicability of the approach.

## **Annual Progress Report**

### **2001 Progress Report**

# **Environmental Management Science Program Research in Washington**

## **Pacific Northwest National Laboratory**

### **73758 – Fixations Mechanisms and Desorption Rates of Sorbed Cs in High Level Waste Contaminated Subsurface Sediments: Implications to Future Behavior and In-Ground Stability**

**Principal Investigator:** Dr. John M Zachara

**Problem Area:** Subsurface Contamination

Research will extend scientific understanding of Cs geochemistry and newly developed single-particle manipulation/analytical capabilities resulting from a FY 97 EMSP project to investigate the geochemical behavior of  $^{137}\text{Cs}$ -contaminated sediments collected from beneath leaked single shell tanks at Hanford. The leak events occurred 25-35 years ago, and the study of these materials allows a unique opportunity to define long-term fixation processes and their implication to future migration. Our goals are to define the mineralogic residence and intra-particle distribution of  $^{137}\text{Cs}$  in sediments contaminated with two different high-level waste (HLW) types, and to define the relationships of residence and distribution to  $^{137}\text{Cs}$  desorbability and exchange with the aqueous phase.

Contaminated sediments that vary in  $^{137}\text{Cs}$  content and HLW-induced mineral transformation will be studied from boreholes beneath leaked tanks SX-108 and BX-102. Microparticle manipulation and analytical techniques {low level gamma counting, digital autoradiography, transmission electron microscopy with energy loss spectroscopy (TEM-ELS), electron microprobe, dynamic and time of flight secondary ion mass spectrometry (SIMS), and synchrotron X-ray microspectroscopy} will be applied to isolate and quantify external/internal spatial distribution of Cs in the contaminated particles. Laboratory-spiked Hanford micas will be used also as model phases. Desorption kinetic studies will be performed on model and contaminated sediments with different chemical conditions and a model developed that links kinetic behavior with Cs containing particle characteristics. Improved conceptual and numeric models of the future geochemical behavior of sorbed Cs in the vadose zone will result that are needed to develop credible remediation and closure plans for Hanford's highly contaminated tank farms.

## **Annual Progress Report**

**2001 Progress Report**

**2002 Progress Report**

# Environmental Management Science Program Research in California

## Lawrence Berkeley National Laboratory

### 73773 – Isotopic Tracers for Waste Fluid Tracking and Fluid-Soil Interactions: Hanford, Washington

**Principal Investigator:** Dr. Donald J. DePaolo

**Problem Area:** Subsurface Contamination

Isotopic measurements of groundwater at Hanford will be used to evaluate chemical and hydrologic controls on the transport and retention of radionuclides in the vadose zone and saturated zone. Isotopic ratios of the elements O, C, N, H, Sr, and U will be made on groundwater collected on the normal sampling schedule of the ongoing Groundwater Monitoring program, with some supplementary sampling. A comprehensive site wide database will be assembled that will represent the most complete isotopic characterization ever undertaken for an aquifer. More detailed sampling will concentrate on the 200 Areas, in particular the areas near and downstream from single shell tank farms. The results are expected to be a major augmentation to standard groundwater characterization, and will be sufficiently detailed to allow us to fully evaluate the potential of naturally occurring isotopic variations to understand groundwater and contaminant migrations. The Hanford site is ideal for the proposed study because of the number of regularly sampled groundwater wells, large isotopic contrasts between introduced waste fluids and natural groundwater, and the amount of other spatial and historical data that can be drawn upon. Sufficient preliminary work has been done as part of a previous EMSP grant to confirm the feasibility of the proposed study.

The results of this study will yield information that is critical for developing improved conceptual models for vadose zone and groundwater transport of radionuclides and other contaminants of concern. In particular, the isotopic tracing techniques allow us to track the movement of waste fluids, which is a significant augmentation to the use of contaminants to trace plumes, since the source term for the contaminants is more complicated than that for the waste fluids. Data from groundwater samples downstream from single shell tanks and other concentrated waste disposal sites, will allow us to evaluate the extent of chemical reactions between concentrated waste fluids and subsurface soils in the vadose zone. These reactions, which are hypothesized to occur but remain undocumented, may greatly modify the transport of radionuclides through the vadose zone beneath tanks.

The proposed research addresses research needs for characterization and transport validation in soils, and for hydrologic and chemical effects on contaminant infiltrations rates through the vadose zone. Relevant Subsurface Contamination needs statements are

- *RL-229-S: Effect of Subsurface Heterogeneities on Chemical Reaction and Transport*
- *RL-SS27-S: Rates of Coupled Abiotic and Biogeochemical Reactions Involving Contaminants In Hanford Subsurface.*
- *RL-SS26-S: Reaction Rates for Key Contaminant Species and Complexes in Site-Specific Groundwaters.*
- *AL-09-01-14-SC-S: Vadose Zone Flux Rates*
- *RL-SS35-S: Use of Chemical Surrogates for Contaminant Monitoring*
- *RL-SS35-S: Use of Chemical Surrogates for Contaminant Monitoring*

The proposed work is synergistic with ongoing studies of groundwater and vadose zone processes being carried out as part of the Hanford Groundwater-Vadose Zone Integration Project (GW/VZ) and by the River Protection Program. During the period of performance of this grant, there will be concurrent studies of the isotopic geochemistry of Hanford soils and vadose zone fluids in the 200 West area, and infiltration tests that will include O, D, and Sr isotopic tracers. Our results from the groundwater analyses will aid interpretation of the data from the vadose zone, and the studies of the vadose zone samples and infiltration tests will be critical to our interpretations of groundwater data.



## **Annual Progress Report**

### **2001 Progress Report**

# **Environmental Management Science Program Research in California**

## **Lawrence Berkeley National Laboratory**

### **73775 – Colloid Genesis/Transport and Flow Pathway Alterations Resulting From Interactions of Highly Reactive Waste Solutions and Sediments in the Vadose Zone**

**Principal Investigator:** Dr. Jiamin Wan

**Problem Area:** Subsurface Contamination

The objectives of this proposed research are twofold. The first is to understand the mechanisms controlling reaction-induced colloid formation, remobilization, and transport in vadose environments, and to identify the nature and quantity of mobile colloids which actually contribute to enhancing contaminant transport under the Hanford Site conditions. The second objective is to identify the physical basis for predicting reaction-induced permeability changes and flow path alterations, and their impact on contaminant plume migration. The specific tasks are listed below.

1. Determine the mechanisms, nature and quantity of particle generation, and its dependence on waste solution chemistry, sediment chemistry, mineralogy and surface chemistry, and temperature during waste fluid infiltration into Hanford sediments.
2. Quantify the combinations of matric potential, flow rate, and solution chemistry (composition, ionic strength and pH), required to remobilize previously attached colloids.
3. Quantify colloid transport and deposition (filtration) under vadose zone conditions through accounting for influences of matric potential, colloid properties, and solution chemistry.
4. Quantifying and predict saturated and unsaturated hydraulic conductivity changes, and consequent changes in vadose zone flow paths.

To achieve these goals we will continue to test the Hanford Formation sediment used in our current study (containing a moderately wide range of grain-sizes), and select certain size fractions if necessary. The same simulated REDOX Tank Waste solution (TW) used in our current study, based on the composition of single shell tank SX-111, will be used. We may also alter the composition within the range of Agnew's (1995, 1996) estimation. The chemical composition of the infiltration soil solution will be based on the water extract composition of the Hanford sediment, with the sediment:water ratio of 1:05 to 1:10, to simulate deep vadose zone pore waters and near surface pore waters, respectively. For studies of colloid generation (task 1), the column method used in our current Hanford research will be used (see attached report). A method designed for studies of colloid remobilization (task 2) is illustrated in figure B3 of this proposal. For studies of unsaturated colloid transport (task 3), the method specially developed for this purpose (Wan and Tokunaga, 1997) will be used. To study flow path alteration (task 4), waste infiltration experiments will be conducted into 2- and 3- dimensional vadose sediment containers. Our laboratory is well equipped with the capabilities of colloid characterization such as size distribution, and surface charge. Analytical electron microscopy and will be used to quantify the chemical composition, mineralogy, morphology, and crystallinity of colloids. We have access to the National Center for Electron Microscopy (LBNL).

## **Annual Progress Report**

### **2001 Progress Report**

### **2002 Progress Report**

# **Environmental Management Science Program Research in California**

## **Lawrence Berkeley National Laboratory**

### **73776 – High Frequency Electromagnetic Impedance Measurements for Characterization, Monitoring and Verification Efforts**

**Principal Investigator:** Dr. Ki Ha Lee

**Problem Area:** Subsurface Contamination

We propose to continue development of high-frequency impedance (HFI) methodology utilizing a window in the electromagnetic (EM) spectrum from 1.0 MHz to 100 MHz. This window, located between GPR and low-frequency induction techniques, has not been used to non-invasively investigate the upper few meters of the ground for environmental applications. Modeling and physical parameter studies confirm that impedance measurements in this frequency band can yield high-resolution mapping of electrical conductivity as well as the permittivity of near surface formations. In principle the impedance method we propose is free of source coupling for plane waves, so that the ensuing data analysis tends to be much simpler.

The proposed research plan consists of three tasks: 1) continued development and completion of high-frequency field measurement techniques, 2) construction and delivery of a field-hardened prototype HFI system, and 3) data processing, analysis, and interpretation. The proof-of-concept for the HFI system has been demonstrated in the first phase of the research program (1997 through 2000). Construction of a mobile HFI field system can be accomplished using off-the-shelf instrumentation and commercially available components, but research will be continued to develop better high-frequency sensors using innovative designs. Development of an analysis package for processing and interpretation of high-frequency data is also an essential part of the proposed work. Towards the end of the project, the prototype system will be capable of real-time mapping of the electrical conductivity and permittivity using simultaneous inversion in one dimension. Feasibility for implementing higher-dimensional analysis package in field operation will be critically evaluated.

## **Annual Progress Report**

**2001 Progress Report**

**2002 Progress Report**

# Environmental Management Science Program Research in Tennessee

## Oak Ridge National Laboratory

### 73784 – Microbially Mediated Immobilization of Contaminants Through *In Situ* Biostimulation: Scale up of EMSP project 55267

**Principal Investigator:** Dr. Phillip M. Jardine

**Problem Area:** Subsurface Contamination

The overall goal of the proposed research is to provide an improved understanding and predictive capability of the mechanisms that allow metal-reducing bacteria to be effective in the bioremediation of redox sensitive toxic metals and radionuclides. The study is motivated by the likelihood that subsurface metal-reducing bacteria can be stimulated to effectively alter the redox state of contaminants so that they are immobilized *in situ* for long time periods. The work described in this proposal will advance the technological and scientific needs associated with the long-term management of the enormous in-ground inventories of Cr, U, Tc, and Co present at numerous DOE installations throughout the country. The objectives of our project are to (1) develop an improved understanding and predictive capability of the rates and mechanisms controlling microbially mediated reduction of toxic metals and radionuclides and metals *in situ*, (2) quantify the impacts of hydrological and geochemical processes on the effectiveness of indigenous microorganisms to transform and immobilize radionuclides and metals *in situ*, (3) provide an improved understanding of the importance of microbial consortia interactions in the bacterial immobilization of radionuclides and toxic metals, and (4) determine intrinsic bioreduction rate parameters to improve our generic predictive capability of *in situ* microbially mediated metal reduction. Our approach involves a multiscale experimental and numerical endeavor that uses (1) undisturbed cores and a well-characterized, highly instrumented field facility for assessing biostimulation remedial strategies involving Cr(VI), U(VI), and Co(III)EDTA, (2) multiple tracer techniques designed to delineate the influence of coupled hydrological, geochemical, and microbial processes, (3) a novel microarray-based genomic technology for rapidly characterizing shifts in microbial community structure and activity, (4) sophisticated surface analysis techniques (x-ray absorption spectroscopy) for quantifying the distribution and chemical environment of the immobilized contaminants, and (5) next-generation, high-performance hydrobiogeochemistry modeling to assist the design and performance assessment of the proposed field scale experiment. The experimental and numerical results from this research will provide knowledge and information in previously unexplored areas of *in situ* biostimulation for metal and radionuclide immobilization to support EM's mission of long-term isolation and *in situ* remediation of contaminated environments. By unraveling the fundamental mechanisms controlling the microbially mediated reduction and immobilization of contaminants *in situ*, we provide an enhanced opportunity for successfully implementing biostimulation strategies at numerous DOE installations that are plagued with legacy waste. Further, this proposal combines DOE's commitment to environmental restoration with its commitment to major user facilities (SSRL, high-performance computing) and academic education.

## Annual Progress Report

### [2001 Progress Report](#)

### [2002 Progress Report](#)

# Environmental Management Science Program Research in Tennessee

## Oak Ridge National Laboratory

### 73793 – Biofiltration of Volatile Pollutants: Solubility Effects

**Principal Investigator:** Dr. Brian H. Davison

**Problem Area:** Subsurface Contamination

This project will investigate and collect fundamental partitioning data for a variety of sparingly soluble subsurface contaminants (e.g., TCE, etc.) between vapor, aqueous phase, and matrices containing substantial quantities of biomass and biomass components. Due to the difficulty of obtaining these measurements, environmental models have generally used solubility constants of chemicals in pure water or, in a few rare cases, simple linear models. Our prior EMSP work has shown for two sparingly soluble organics that the presence of biological material can increase effective solubilities by an order of magnitude; therefore, the previous simple approaches are not valid and are extremely poor predictors of actual bio-influenced partitioning. It is likely that environmental contaminants will partition in a similar manner into high-biomass phases (e.g. biobarriers and plants) or humic soils. Biological material in the subsurface can include lipids, fatty acids, humic materials, as well as the lumped and difficult to estimate 'biomass'. Our measurements will include partition into these biological materials to allow better estimation. Fundamental data collected will be provided to mathematical models predicting transport and sorption in subsurface environments, with the impacts on bioremediation being evaluated based on this new information. Our 2-D Win95/98 software program, Biofilter 1.0, developed as a part of our prior EMSP efforts for describing biofiltration processes with consideration given to both kinetic and mass transfer factors, will be extended to incorporate and use this information.

This research will provide much-needed fundamental information regarding partitioning of priority contaminants in subsurface aquifers, vadose zones, and surface water impoundments where biological material is present. Accurate data measurements of phase distributions of sparingly soluble organics between biomass/water/air are needed to replace the current assumptions using pure water data. Beyond the detailed equilibrium measurements of a variety of contaminants and biomaterial types, we also will seek to characterize the materials in order to understand the fundamental properties that cause different biological materials to have different partition constants.

Specifically,

- 1) Partition solubilities will be measured experimentally for volatile priority pollutants (TCE, PCE, CCl<sub>4</sub>, BTEX) in biomaterial/air and biomaterial/water/air systems (Henry's law constants and aqueous/biomaterial partition constants). These measurements will be conducted in sealed, gas-tight vessels (see Figure 5) and consist of simultaneous equilibrium concentration values of organics in the three phases: liquid, biomaterial, and vapor.
- 2) Partition constants of priority contaminants (as above, plus PAHs, etc.) in aquifer matrices containing varying levels of biological material will be measured experimentally under different geochemical conditions of pH, ionic strength, etc. These measurements will consist of simultaneous equilibrium concentration values of organic contaminants in four phases: liquid, biomaterial, vapor, and solid support.
- 3) Compositional analysis. The effect of key components (lipids, proteins, polysaccharides, fatty acids) that are commonly lumped together as "biomass" will be analyzed, along with cell hydrophobicity, to understand the underlying mechanisms for these partition differences. Representative types of biomass will also be used [e.g., microbial, degradative consortium, plant material (plant root tips) bacteria, yeast, etc.] to help validate compositional isotherms. Prior literature analyses have only used total organic carbon content as a potential sorption predictor.

- 4) Constitutive relationships to enable these data to be used in standard fate and transport of bioremediation models will be developed, validated, and distributed.
- 5) These partitioning constants will allow more accurate predictions of fate and transport of pollutants wherever biological material is present. Aqueous/biomaterial results will be applicable to subsurface groundwaters/aquifers and to waterways with contaminated sludge layers, while vapor/biomaterial results will apply to subsurface vadose zones and surface water impoundments.
- 6) Biofilter 1.0 software will be extended to incorporate the information above. This program, developed for EMSP 55013, is publicly available at <http://www.ct.ornl.gov/biofilter>.

## **Annual Progress Report**

### **2001 Progress Report**

### **2002 Progress Report**

## **Environmental Management Science Program Research in Tennessee**

### **Oak Ridge National Laboratory**

#### **73808 – Microsensors for In-Situ Chemical, Physical, & Radiological Characterization Mixed Waste**

**Principal Investigator:** Dr. Thomas G. Thundat

**Problem Area:** Subsurface Contamination

A widespread need exists for portable, real-time, in-situ chemical, physical, and radiological sensors for the characterization and monitoring of mixed waste, ground water, contaminated soil and process streams ranging from plume containment and remediation to determination of location, chemical composition, and level of DNAPLs. In the first phase of this EMSP program, we have successfully demonstrated sensitive microcantilever sensors for solution with unprecedented sensitivity. However, the molecular level mechanism responsible for sensor action still remains poorly understood and this limits our ability to rationally design more sensitive and selective sensors for variety of target analytes especially when more than one analyte is present.

The objective of this research phase is to gain a better understanding of the molecular-level mechanism of adsorption-induced stress on the microcantilever. The ability to manipulate and control these stresses will lead to the development of highly selective and extremely sensitive sensors for EM specific applications in liquid environment in presence of interferents. For example, it is possible to separate chemisorption and physisorption by simultaneous measurement of resonance parameters. Based on this fact, we will develop and demonstrate corrosion resistant cantilevers with parts-per-trillion sensitivity for metal ions in solution such as  $\text{Hg}$ ,  $\text{CrO}_4^{2-}$ ,  $\text{Sr}^{2+}$ , and  $\text{TcO}_4^-$ . Selectivity will be achieved by orthogonal arraying of modified cantilevers. In addition, we will also develop microcantilever radiation sensors that can operate under solution.

We plan to bring the proposed prototype sensors to a stage where they will be field-tested in the third year. The advantage of the cantilever sensors is that once the basic platform is developed, it can be the basis for a plethora of inexpensive, miniature sensors.

### **Annual Progress Reports**

#### **2002 Progress Report**

# Environmental Management Science Program Research in New Mexico

## Sandia National Laboratories - Albuquerque

### 73812 – Physics of DNAPL Migrations and Remediation in the Presence of Heterogeneities

**Principal Investigator:** Dr. Stephen H. Conrad

**Problem Area:** Subsurface Contamination

Spilled solvents have created pervasive groundwater contamination problems across the DOE complex because of their ubiquitous use, their toxicity and persistence in the environment, combined with the difficulty of recovering them from the subsurface. Because organic solvents are more dense than water and immiscible with water, they are commonly referred to as DNAPLS (dense non-aqueous phase liquids). They migrate below the water table downward and laterally under the influence of gravity, capillary, and viscous forces. Variations in media texture that the DNAPLS encounter as they migrate can have a profound influence on the migration path. This interplay between textural heterogeneities and driving forces complicates the migration of the DNAPLS and therefore it is not straightforward to predict the locations in the aquifer at which the spilled DNAPLS may ultimately reside. Uncertainties in the region of solvent contamination translate into higher remediation costs as the remedial system must be designed in light of these uncertainties. In an effort to clean up spilled DNAPLS, several remediation approaches are currently under development. Chemically enhanced solubilization, alcohol displacement, in situ oxidation, and air sparging are among the most promising. Many of these techniques have already undergone preliminary field demonstrations. However, results from such field demonstrations cannot be extrapolated to predict remedial performance under the wide range of field conditions to be encountered at spill sites across the DOE complex. Indeed, these techniques have not yet had the opportunity to be sufficiently tested and quantitatively compared in well-controlled laboratory experiments under heterogeneous conditions indicative of what can be expected in the field. In addition, the numerical simulation techniques used to predict DNAPL migration and remediation treatments have yet to be adequately verified through comparison against laboratory experiments conducted in heterogeneous media.

Our research effort funded by *EMSP* has been designed as broad and crosscutting. The goal of our research is to develop a fundamental quantitative understanding of the role of physical heterogeneities on DNAPL migration and remediation in aquifers. Such understanding is critical to cost effectively identify the location of the subsurface zone of contamination and design remediation schemes focused on removing the source of the contamination, the DNAPL itself. There are two major aspects to the DNAPL problem: finding them (migration) and cleaning them up (remediation). In an ambitious research plan, we have been working on both. By designing lab experiments within heterogeneous porous media analogous to field conditions, we have been able to directly observe DNAPL initial migration and subsequent interactions between injected remedial agents and the DNAPL. In these experiments we have identified critical mechanisms having important implications affecting both the initial migration and the successfulness of remedial processes.

For migration, we have found the influence of heterogeneities to yield high DNAPL saturation “pools” of a wide range of sizes, corresponding to the effects imposed by textural variations between geologic facies. These pools are interconnected by fingers where very little DNAPL resides. When viscous forces are low, we discovered the DNAPL structure to pulsate at both the pore scale within fingers and at the unit scale within large pools due to a capillary-gravity pulsation mechanism. We have built pore scale invasion mechanisms into a fundamentally new modeling approach, a for of Modified Invasion Percolation of MIP model. Our simulations yield results that closely track the migration behavior seen in our experiments. IN the continuation of this work we will further explore DNAPL migration in the presence of both macro- and micro-layered heterogeneities. We will closely consider the effects imposed on migration by capillary-gravity pulsation and when significant viscous forces are present as each of these has been found experimentally to yield multiple DNAPL migration pathways. For remediation, we performed both micro-model experiments to elucidate surfactant enhanced mobilization and dissolution mechanisms as well as bench-scale remediation demonstration experiments for two different surfactants and an in situ oxidizer



(potassium permanganate). From our results *we emphasize caution and advocate a restrained approach to site remediation at this time*. In all cases considered so far, the initial configuration of the DNAPL in pools and fingers dramatically influenced the efficacy of the remediation method. In the continuation of this work we will conduct further demonstrations for remediation techniques. However, we intend to focus our effort using the insights gained and models developed from our work on migration to better understanding the conditions in which inadvertent re-mobilization can occur during remediation efforts. We will also focus on improving our representativeness by working with so-called “dirty DNAPLs” – less ideal, more realistic multi-component organic liquids.

## **Annual Progress Report**

### **2001 Progress Report**

# **Environmental Management Science Program Research in New Mexico**

## **Los Alamos National Laboratory**

### **73819 – Plutonium Speciation, Solubilization, and Migration in Soils**

**Principal Investigator:** Dr. Mary Neu

**Problem Area:** Subsurface Contamination

The DOE is currently conducting cleanup activities at its nuclear weapons development sites, many of which have accumulated plutonium in soils for 50 years. There is scientific uncertainty about the levels of risk to human health posed by this Pu accumulation and about whether or not Pu is migrating from Federal reserves onto public lands. To properly control Pu migration in soils, to better evaluate the public risk, and to design effective remediation strategies, a fundamental understanding of Pu speciation, transport, and release mechanisms is needed. Key elements of this proposal are listed below:

- Determination of Pu distribution, oxidation state(s) and speciation in select soil samples from two contaminated sites-Hanford and INEEL. The speciation and additional characterization of Pu in these soils will aid in the remediation of these sites, assist in the understanding of Pu at other sites, and increase our understanding of actinide environmental chemistry. Once characterization is complete, Pu will be added to the samples to learn how additional Pu interacts with the specific matrix, i.e. is it reduced or oxidized and/or sorbed to particular phases.
- Study of chemical systems most important in Pu environmental behavior. This will provide critical thermodynamic data, as well as structural and chemical models, for environmental samples. Past literature on environmental sample characterization have reported the predominance of Pu(V) in sea and groundwaters and recent literature and waste isolation simulation studies have suggested the potential importance of Pu(VI) and colloidal Pu(IV). The speciation and redox chemistry of Pu(V) and Pu(VI) and the stability and migration of real and pseudo Pu(IV) colloids under environmentally relevant conditions will be investigated.
- Determination of the mechanism and thermodynamics of interactions between Pu and Mn phases and the potential release of Pu via redox cycling. Pu has been postulated and shown to be associated with redox active minerals, i.e. Fe and Mn (oxy)hydroxides and oxides. Pu association with particular minerals within samples from contaminated sites will be examined. This will provide information on the possible geochemical transformations and reactions with redox active minerals presently not understood.

## **Annual Progress Report**

[2001 Progress Report](#)

[2002 Progress Report](#)

# Environmental Management Science Program Research in Massachusetts

## Massachusetts Institute of Technology

### 73836 – Induced Polarization with Electromagnetic Coupling: 3D Spectral Imaging Theory and Field Tests

**Principal Investigator:** Dr. Frank Dale Morgan

**Problem Area:** Subsurface Contamination

The Earth Resources Laboratory (ERL) has made recent advances in applying the Induced Polarization (IP) method for detection and mapping of contaminant plumes. The ERL has developed a 3D complex resistivity and time-domain inversion codes, and performed modeling which shows that SIP requires a wide frequency range to be effective. Laboratory experiments have revealed that the greatest IP response to contaminants is at frequencies higher than 1KHz. However emc limits the effective frequency range to below 100 Hz, and present correction methods are inadequate. *The project will address the em coupling problem by a fundamentally new approach; we will directly include em induction in the IP modeling inversion codes.* In other words, we will treat the electromagnetic coupling (emc) as a data signal, with useful information about the conductivity structure, instead of as a useless noise signal.

A forward problem is to be developed which predicts both the IP and the em part of the data from a model. An appropriate inverse algorithm will be developed for 3D spectral IP field data. The new modeling will incorporate rather than eliminate em inductive coupling, extending the effective frequency range of SIP to the region of greatest interest beyond 1KHz. The new method will also increase the subsurface resolution of tomography as the em component of the data is fused with IP, where the em is sensitive to the conductivity structure. The project will also perform two field demonstrations of SIP and time domain IP at two sites.

The original DOE project (DE-FG0296ER14714) was a broad foundational study of spectral IP (SIP) for site characterization. The project encompassed laboratory studies of microgeometry and chemistry effect on Induced Polarization (IP), an investigation of (emc) noise, and development of 3D modeling and inversion codes. *The project showed that emc is the major limitation for field implementation of SIP and conventional correction methods are inadequate.* The present project is more focused, with the aim of resolving the em coupling problem to enable inversion of spectral data in the desired higher frequencies above 1 KHz. The approach is to couple IP and em in the modeling and inversion based on Maxwell's questions. The objectives of the renewal project are

- *Extend the present 3D codes to include coupled IP-EM modeling & inversion*
- *Demonstrate field applications of 3D SIP and time domain IP at two DOE sites.*

**This project began in 2001. The first progress report is expected in late 2003.**

# Environmental Management Science Program Research in California

## University of California at Davis

### 73843 – Mechanisms of Heavy Metal Sequestration in Soils: Plant-Microbe Interactions and Organic Matter Aging

**Principal Investigator:** Dr. Teresa W-M. Fan

**Problem Area:** Subsurface Contamination

The myriad of human activities including strategic and energy development at various DOE installations have resulted in the contamination of soils and waterways that can seriously threaten human and ecosystem health. Development of efficacious and economical remediation technologies is needed to ameliorate these immensely costly problems. Bioremediation (both plant and microbebased) has promising potential to meet this demand but still requires advances in fundamental knowledge. For bioremediation of heavy metals, the three-way interaction of plant root, microbial community, and soil organic matter (SOM) in the rhizosphere is critically important for long-term sustainability but often unconsidered. Particularly urgent is the need to understand processes that lead to metal ion stabilization in soils, which is crucial to all of the goals of bioremediation: removal, stabilization, and transformation. This renewal proposal will build on the knowledge that we have generated on the role of root exudation and metabolism for metal mobilization and accumulation, to address the following objectives:

1. Identify molecular markers and characterize the chemical nature of recalcitrant SOM pools that are involved in belowground metal ion interactions, which are likely to be markers for sustainable sequestration;
2. Utilize 1) to determine plant and microbial factors that contribute to sustainable metal sequestration or mobility, as well as bioavailability;
3. Utilize information from 1) and 2) to explore efficacious means for enhancing sustainable phytostabilization of heavymetals in the subsurface zone.

To achieve these objectives, we will conduct aging experiments using  $^{13}\text{C}$ -enriched plant matter with or without Cd, Pb, Sr, and Cs loading to trace the turnover of various organic components, and to discern chemical markers that represent recalcitrant SOM involved in interactions with heavy metal ions. The principal approach employed for this task are *in situ* organic chemical fingerprinting and turnover time measurements of whole soils by pyrolysis gas chromatography-mass spectrometry (py-GCMS) and py-GC combustion isotope ratio MS (py-GC-CIR-MS). The age markers thus obtained will be differentiated for relation to metal ion bundung by characterizing metal ion-induced chemical changes in major recalcitrant SOM (i.e. humate and humin) using py-GCMS, NMR, FT-IR, and 3-D flourescene. In turn, these metal ion-associated chemical markers will be used to follow the effect of active plant growth (involving mainly root exudation and architecture), attendant changes in microbial community, and soil aging on heavy metal stabilization, leachability, and bioavailabilty to plants. If time permits, we will also apply the approach to examine the influence of various organic residues (e.g.crop residues) on metal ion mobility and sequestration. The materials of interest are common non-polluted materials for soil cover or amendment, differing widely in organic compositions (e.g. lignin, cellulose, proteins, or pectin) which, upon diagenesis to SOM, may yield various levels of enhancement for metal sequestrian capacity.

If successful, this research should lead to fundamental advances in the understanding of plant-microbe interactions and how these interactions govern the long-term fate of heavy metals in belowground ecosystems. There should be direct applicability of these tools and knowledge to facilitate and enhance field implementation and monitoring of metal bioremediation.

**This project began in 2001. The first progress report is expected in late 2003.**

# **Environmental Management Science Program Research in Washington**

## **University of Washington**

### **73858 – Chlorinated Hydrocarbon Degradation in Plants: Mechanisms and Enhancement of Phytoremediation of Groundwater Contamination**

**Principal Investigator:** Dr. Stuart E. Strand

**Problem Area:** Subsurface Contamination

The goals of our research are to improve the efficiency and applicability of phytoremediation of chlorinated hydrocarbons (CHC's) by acquiring a fundamental understanding of the transformation mechanisms in plants and by using that knowledge to increase CHC degradation in the plants by genetic engineering. One of the limitations of phytoremediation—its requirement for large amounts of land—may be overcome by genetically engineering trees with increased degradative potential for CHCs. We plan to approach this goal in three ways: 1) by introducing foreign genes for CHC degradation, e.g., mammalian cytochrome P450 2E1, 2) by determining the mechanism of CHC degradation in plants, and 3) by increasing the expression of the genes in plants responsible for the oxidation of CHCs. We have made progress toward these goals in our previous EMSP funding period. Transgenic plants containing introduced mammalian cytochrome P450 2E1 genes have greatly increased CHC degradative capacity. Biochemical assays suggest that a plant enzyme very similar to the mammalian cytochrome P450 2E1 is involved in CHC degradation. Our research objectives are to transform poplar and other tree species to optimize their CHC oxidative activities, to determine the mechanism of CHC oxidation in plants by improved culture techniques and by testing of alternative hypotheses, and to isolate the genes responsible for CHC oxidation in plants.

#### **Goals**

Our goals are to improve the efficiency, range of application, and economics of phytoremediation of chlorinated hydrocarbons (CHCs) in vadose zone soils and groundwaters. Our research objectives are as follows:

1. Transform poplar and other tree species to extend and optimize CHC oxidative activities.
2. Determine the mechanisms of CHC oxidation in plants.
3. Isolate the genes responsible for CHC oxidation in plants.

#### **Annual Progress Reports**

##### **2002 Progress Report**

## Environmental Management Science Program Research in Alabama

### University of Alabama

#### **73914 – Reductive Immobilization of U(VI) in Fe(III) Oxide- Reducing Subsurface Sediments: Analysis of Coupled Microbial–Geochemical Processes in Experimental Reactive Transport Systems**

**Principal Investigator:** Eric E. Roden, Ph.D.

**Problem Area:** Subsurface Contamination

The subject matter of this proposal pertains to the Environmental Restoration Focus Area within the scope of current EMSP Science Needs, and to the Biogeochemistry and Geochemistry sections within this Focus Area.

The new project will apply findings and experimental techniques developed during previous EMSP- funded research on the microbiological and geochemical controls of bacterial Fe(III) oxide reduction to an analysis of the reductive immobilization of aqueous U(VI) species in Fe(III) oxide-reducing subsurface media. This line of research is a logical extension of the original Rodin/Urrutia EMSP 96-10 grant. The purpose of our original request for funding to conduct basic research on microbial Fe(III) oxide reduction was to develop experimental techniques and a knowledge base that could be used for future studies of metal-radionuclide transformations which are either directly coupled to or strongly influenced by microbial Fe(III) oxide reduction. We have made substantial progress toward this goal, and are prepared to pursue research related to metal-radionuclide remediation involving Fe(III) oxide-reducing bacteria.

The project will address several basic questions related to the interaction between microbial reduction of Fe(III) oxides and U(VI) in experimental reactive transport systems. These studies will provide information required to evaluate and predict the potential effectiveness of *in situ* redox barrier technologies for metal-radionuclide immobilization. In order to comprehensively examine such interactions, the research team has expanded to include investigators from Auburn University (Auburn, AL) and Pacific Northwest National Laboratory (Richland, WA). The major lines of investigation to be pursued by the different organizations will benefit from the corresponding investigator's extensive past research experience and technical knowledge. The PI's main areas of expertise are the anaerobic biogeochemistry and regulation of metal oxide reduction activity in soils and sediments, the physiology and ecology of anaerobic respiratory bacteria, and transport-reaction modeling of microbial processes in anaerobic sediments. Co-PI Urrutia has extensive experience with the cultivation of metal-reducing bacteria and design/execution of metal-reduction experiments; she also has long-standing experience in metal sorption to soils and bacteria. Co-PI Barnett is an aquatic chemist with expertise in the environmental chemistry of trace and contaminant metals, specifically including uranium. He will provide the main source of information and guidance regarding interpretation of the aqueous and solid-phase geochemical behavior of uranium in our experimental systems. He will also provide critical input to geochemical aspects of the simulation modeling to be conducted in the project. Co-PI Lange is an environmental engineer with extensive experience in contaminant fate and transport in environmental systems, particularly as they are regulated by microbial activity. (note his B.S. degree in Microbiology.) He is a specialist in the use of column reactor technology for studies of contaminant transformation. Dr. Gorby is an expert in bacterial mineral formation (biomineralization), and is a leader in the application of novel electron microscopic techniques for assessing the abundance and spatial distribution of biogenic materials in bacterial cell-particle surface interfacial environments. This unique combination of research expertise brought together in this project will provide information critical for the future development of *in situ* uranium bioremediation strategies at DOE sites.

### Annual Progress Reports

#### 2002 Progress Report

## **Environmental Management Science Program Research in Texas**

### **Rice University**

#### **73962 – Advanced High Resolution Seismic Imaging, Material Properties Estimation and Full Wavefield Inversion for the Shallow Subsurface**

**Principal Investigator:** Dr. Alan Levander

**Problem Area:** Subsurface Contamination

Seismic methods have the potential to fully depict the contours and connectivity of subsurface aquitards and other essential structure for design of groundwater remediation programs. Use of seismic imaging methods thus promises to reduce the level of uncertainty about contaminant pathways due to the necessary scarcity of test wells and the untestable assumptions of geostatistical interpolation methods.

We are requesting a one year renewal of this contract to complete development and testing of an integrated suite of imaging and inverse techniques for 2-D and 3-D seismic data that we are developing for shallow high resolution imaging. An extremely important part of the renewal is to complete analysis of a 3-D seismic survey at a Superfund site which we will undertake in July- August 2000.

Seismic analysis development has included 2-D Kirchhoff inversion, 2-D depth focusing analysis, 2-D wavefield inversion, and 2-D and 3-D travel time tomography. Work under the renewed contract will extend Kirchhoff inversion, depth focusing, and full waveform inversion methods to 3D. We will apply both conventional analysis methods as well as these advanced analysis methods to 3D survey data we will have acquired as part of this project.

To date we have conducted a number of high resolution seismic surveys including one extremely successful 2-D experiment at the Operable Unit 2 Superfund site at Hill Air Force Base, Utah, and a test 3-D survey at Rice University. We have a 3-D seismic experiment planned at OU-2 at Hill AFB for July-August 2000. This survey is designed to make a three dimensional map of a shallow paleo-channel along which DNAPLs are confined at the base of a shallow aquifer.

This request is for personnel costs to complete software development and data analysis of the 2-D and 3-D seismic data. The 3-D seismic data acquisition costs are included in the original proposal. We note that we had intended to complete the 3-D survey in the summer of 1999, however the high-frequency instrumentation needed for the survey was unavailable before the weather window closed in 1999. Delay of the survey has resulted in a considerably larger number of instruments to use for this survey. IRIS PASSCAL have added 200 additional instruments to the pool available, so that we will now conduct the survey with about 700 seismic channels. We have also recently conducted a test 3-D survey at Rice as a shakedown exercise for the 3-D experiment this summer.

### **Annual Progress Report**

**2001 Progress Report**

**2002 Progress Report**

# **Environmental Management Science Program Research in Idaho**

## **Idaho National Engineering and Environmental Laboratory**

### **86598 – Coupled Flow and Reactivity in the Variably Saturated Porous Media**

**Principal Investigator:** Dr. Carl Palmer

**Problem Area:** Subsurface Contamination

Improved understanding of contaminant migration processes through the vadose zone is required for DOE to provide defensible computational models, better define long-term stewardship requirements for DOE sites, and help design effective barriers to vadose-zone contaminant migrations. We propose research that results in improved conceptual models of contaminant migration in heterogeneous, variably saturated, porous media, particularly at low water contents where information is difficult to obtain using traditional methods. We hypothesize that the reactivity of variably saturated porous media depends on the moisture content of the medium and can be represented by a relatively simple function applicable over a range of scales, contaminants, and media. A key, novel aspect of the proposed research is using the new two-meter radius, geocentrifuge being installed at the Idaho National Engineering and Environmental Laboratory (INEEL). This geocentrifuge experimental approach has two distinct advantages over conventional methods. First, experimental data is collected over much shorter time periods, resulting in a more complete evaluation of various chemical conditions and materials. Second, the increased forces in the geocentrifuge allow experiments to be conducted over a wider range of moisture regimes as compared to conventional methods. The proposed three-year project develops new conceptual models for contaminant adsorption and transport in heterogeneous vadose zone media. Although the results of the proposed research applies to all DOE sites, those with deep vadose zones in arid climates, such as the INEEL, Hanford, the Nevada Test Site, and Yucca Mountain will benefit the most from the work.

**This project began in 2002. The first progress report is expected in late 2003.**



# Environmental Management Science Program Research in Georgia

## University of Georgia

### 86608 – Phytoremediation of Ionic and Methyl Mercury Pollution

**Principal Investigator:** Dr. Richard B. Meagher

**Problem Area:** Subsurface Contamination

Our long-term goal is to enable highly productive plant species to extract, resist, detoxify, and/or sequester the toxic heavy metal mercury. Mercury pollution is a serious, world-wide problem affecting the health of human and wildlife populations, primarily due to the production of methylmercury (MeHg,  $\text{CH}_3\text{Hg}^+$ ) by native bacteria at mercury contaminated wetland sites. MeHg is inherently more toxic than metallic  $\text{Hg}(0)$  or ionic  $\text{HG}(\text{II})$  mercury, and because MeHg is efficiently biomagnified up the food chain, it poses the most immediate threat to animal populations. We successfully engineered two model plants, *Arabidopsis* and tobacco, to use the bacterial *merB* gene, methylmercury lyase, to convert MeHg to less toxic  $\text{Hg}(\text{II})$ , and a highly modified bacterial mercuric ion reductase gene, *merA*, to further detoxify  $\text{Hg}(\text{H})$ , electrochemically reducing it to the least toxic metallic form  $\text{Hg}(0)$ . Plants expressing both MerA and MerB proteins detoxify MeHg in two steps to  $\text{Hg}(0)$ . These plants germinate, grow, and set seed at normal growth rates on levels of MeHg or  $\text{HG}(\text{II})$  that are lethal to normal plants. In our newest efforts with several additional bacterial and plant genes, we successfully engineered plants to resist mercury toxicity by hyperaccumulation and sequestration. Physiological experiments demonstrate these various plants can either transpire  $\text{Hg}(0)$  from leaves or trap  $\text{HG}(\text{II})$  in aboveground tissues. We developed an important set of monoclonal antibody reagents to monitor several gene products and determine the rate limiting steps in these pathways. These genetic deferments are being transferred to several field species (yellow poplar, cottonwood, willow, privet, and rice), and the first field testing of these technologies is underway. Multigene strategies give us tremendous flexibility in designing site-specific mercury remediating plants.

**Our current working hypothesis is that transgenic plants controlling the chemical species, electrochemical state, and aboveground binding of mercury will a) prevent methylmercury from entering the food-chain, b) remove mercury from polluted sites, and c) hyperaccumulate mercury in aboveground tissues for later harvest.** This hypothesis leads to a phytoremediation strategy for mercury that is being tested by focusing our research on the following Specific Aims: (1) to increase the transport of mercury to aboveground tissue by developing a root-specific gene expression system; (2) to test the specificity and capacity of several small peptides for mercury binding and hyperaccumulation in aboveground plant organs; (3) to test the ability of multiple transgenes, when functioning in concert, to enhance resistance and hyperaccumulation (i.e., combining sequences characterized previously as single transgenes); (4) to construct a simple molecular system for creating male/female sterility, allowing engineered grass, shrub, and tree species to be released indefinitely at contaminated sites; (5) to test the ability of transgenic cottonwood and rice plants expressing *merB* and/or *merA* to detoxify  $\text{HG}(\text{II})$  and prevent MeHg release from contaminated water and sediment; and (6) to initiate field testing with transgenic cottonwood and rice for the remediation of ionic mercury and methylmercury. The results of these experiments will provide the phytoremediation of methyl- and ionic mercury by a wide spectrum of deep-rooted fast-growing plants adapted to diverse environments.

### Phytoremediation of Ionic and Methylmercury Pollution

#### Non-Technical Abstract

Phytoremediation is defined as the use of plants to extract, resist, detoxify, and/or sequester toxic environmental pollutants. The long-term goal of the proposed research is to develop and test highly productive, field-adapted plant species that have been engineered for the phytoremediation of mercury. A variety of different genes, which should enable plants to clean mercury-polluted sites are being tested as tools for mercury phytoremediation first in model laboratory plants and then in potential field species.

Several have already been shown to enhance mercury phytoremediation. Mercury pollution is a serious, worldwide problem affecting the health of human and wildlife populations. Environmentally, the most serious mercury threat is the production of methylmercury ( $\text{CH}_3\text{Hg}^+$ ) by native bacteria at mercury contaminated wetland sites. Methylmercury is inherently more toxic than metallic  $\text{Hg}(0)$  or ionic  $\text{Hg}(\text{II})$  mercury, and because it is efficiently biomagnified up the food chain, it poses the most immediate danger to animal populations. We successfully engineered two model plants, *Arabidopsis* and tobacco, to use the bacterial *merB* gene to convert methylmercury to less toxic ionic mercury, and to use the bacterial *merA* gene to further detoxify ionic mercury to least toxic metallic mercury. Plants expressing both MerA and MerB proteins detoxify methylmercury in two steps to the metallic form. These plants germinate, grow, and set seed at normal growth rates on levels of methylmercury or ionic mercury that are lethal to normal plants. Our newest efforts involve engineering plants with several additional bacterial and plant genes that allow mercury resistance by hyperaccumulation. The potential for these plants to hyperaccumulate mercury was further advanced by developing constitutive, aboveground, and root-specific gene expression systems.

In order to advance this mercury phytoremediation strategy, our planned research focuses on the following Specific Aims: (1) to increase the transport of mercury to aboveground tissue; (2) to identify small mercury binding peptides that enhance hyperaccumulation aboveground; (3) to test the ability of multiple genes acting together to enhance resistance and hyperaccumulation; (4) to construct a simple molecular system for creating male/female sterility, allowing engineered grass, shrub, and tree species to be released indefinitely at contaminated sites; (5) to test the ability of transgenic cottonwood and rice plants to detoxify ionic mercury and prevent methylmercury release from contaminated sediment; and (6) to initiate field testing with transgenic cottonwood and rice for the remediation of methylmercury and ionic mercury. The results of these experiments will enable the phytoremediation of methyl- and ionic mercury by a wide spectrum of deep-rooted, fast-growing plants adapted to diverse environments.

## **Annual Progress Reports**

[2002 Progress Report](#)

# Environmental Management Science Program Research in Ohio

## Ohio State University

### 86642 – Semi-Passive Chemical Oxidation Schemes for the Long-Term Treatment of Contaminants

**Principal Investigator:** Dr. Frank W. Schwartz

**Problem Area:** Subsurface Contamination

Through the years, a variety of cleanup technologies have been proposed for ground water at contaminated sites. In many cases, the size and complexity of sites make cleanups costly and technically difficult in terms of meeting cleanup goals. It is not surprising then that focus in cleanup strategies has shifted from costly, active approaches, and aggressive treatments to much less costly and often long-term strategies. Thus, there has been an explosive growth of approaches like natural attenuation, capable of controlling problems at relatively low costs. We expect that in the United States as well as countries around the world that interest in low cost technologies will continue to grow.

As a family, passive and semi-passive technologies are attractive because of the significant advantages in operating for long periods of time with relatively low O&M costs. One example is a reactive barrier system that uses zero-valent iron for treating dissolved plumes. Once the investment is made in the capital cost of the iron wall operating costs are minimal. Another approach is the use of time-release compounds (oxygen-release compounds; hydrogen release compounds) to enhance natural biotransformation processes. Typically, biological stimulation uses lines of wells to deliver treatment chemicals to a DNAPL source area and locally and along the dissolved plume. Compared to other technologies the cost of installing wells and periodically adding treatment chemicals is relatively attractive.

*Our study here proposes to develop a scientific basis for the use of semi-passive, wells-based, chemical oxidation systems for treating chlorinated ethylenes (e.g., PCE, TCE, DCE). In situ chemical oxidation or ISCO schemes involve the addition of a chemical oxidant, like potassium permanganate ( $\text{KMnO}_4$ ), which destroys organic contaminants in a straightforward reaction. There are a variety of published and unpublished examples of ISCO schemes applied to cleanups of solvent spills. Most research demonstrations (e.g., West et al., 1997; Lowe et al, 2002) have been short term in nature, designed as proof-of-concept illustrations of the ability of oxidants to destroy compounds like TCE in the subsurface. Most of the industrial applications, involve fixed term, active treatments of a contaminated plume. Without source control ISCO, like pump-and-treat or other technologies, is at a permanent remedy. We think that ISCO schemes have the potential to be developed as low cost, semi-passive approaches for the long-term control and cleanup of contaminated sites. Although ISCO is now regarded as a developing technology in an industrial sense, it has not been researched extensively. For example, beyond active flooding schemes, there have been relatively limited investigations in how ISCO might be better used. In addition, with an active flooding approach, plugging with  $\text{MnO}_2$  can destroy the efficiency of the system with time (Li and Schwartz, 2000).*

This study aims to provide basic research on a new passive remediation concept with ISCO. In essence, solids will be added to wells for dissolution and slow release into ground water. *The first objective is to use laboratory experiments and computer simulations to develop a new passive well-delivery system for the controlled release of  $\text{KMnO}_4$ . A system is required to facilitate the slow release of  $\text{KMnO}_4$  into flowing ground water in a manner that maximizes the lateral spreading, and minimizes the number of wells. We also propose to consider the role of well distribution in maximizing the performance of the system. The second objective is to use laboratory experiments to assess whether chemical mixtures or cyclic chemical renovation schemes are capable of providing both contaminant destruction and plugging control. Preliminary experiments have identified compounds capable of delaying precipitation or dissolving precipitates. We have hopes that even with a passive scheme that plugging can be controlled in the immediate vicinity of wells. The third objective is to evaluate the kinetics of interactions among treatment chemicals and the porous medium in order to optimize design. It is well known that natural, oxidizable*

*compounds in aquifer materials utilize  $KMnO_4$ .* The design of the well-delivery system will require knowledge concerning the fate and transport of  $KMnO_4$ .

**This project began in 2002. The first progress report is expected in late 2003.**

# **Environmental Management Science Program Research in New Mexico**

## **Los Alamos National Laboratory**

### **86679 – Field-Scale In Situ Measurements of Vadose Zone Flow and Transport Using Multiple Tracers at INEEL Vadose Zone Research Park (VZRP)**

**Principal Investigator:** Dr. Robert C. Roback

**Problem Area:** Subsurface Contamination

Processes that influence flow and transport of contaminants through the vadose zone remain poorly understood; despite the fact that the vast majority contaminated sites nationally and globally are in the vadose zones. As a result, large uncertainties in contaminant transport rates typically exist for many sites. Realistic, field scale transport data are needed to lower these uncertainties and provided greater defensibility in DOE decisions on remedial actions and site closures.

This study is aimed at obtaining a better understanding of vadose zone flow and transport processes at the field scale and establishing defensible links between laboratory- and field-derived transport parameters for conservative and reactive elements in the vadose zone. The study site is the Vadose Zone Research Park (VZRP), located at Idaho National Engineering and Environmental Laboratory (INEEL). INEEL has a thick vadose zone and is the site of numerous surface and shallowly buried waste storage sites, some of which are known to have leaked contaminants to the vadose zone. Most of these contaminated sites are within 101 yards of the study site and share a common geologic and hydrologic setting. The research park provides a three-dimensional instrumentation array strategically surrounding a new infiltration pond slated for initial use in the upcoming year, and the Big Lost River, and intermittent stream proximal to the infiltration ponds. The proposed study will leverage cost and effort to establish the VZRP as well as past experience gained from colloid and tracer transport studies conducted for YMP/NTS to develop a well-constrained data set that is highly relevant to contaminant transport in the vadose zone. The proposed study will provide important data to help understand contaminant transport both locally and globally.

The proposed research will utilize planned filling of the infiltration ponds as well as flow in the Big Lost River to study the effects of fluid flux, water chemistry and degree of saturation on contaminant transport in the vadose zone, and physical and chemical interactions between the vadose and saturated zones. Our research plan has four major objectives: 1) to determine the transport of conservative and reactive solute tracers and colloid tracers through the vadose zone, local perched water zones and into the aquifer at VZRP; 2) to examine isotopic variations of U and Sr and compare these to introduced sorbing and non-sorbing tracers; 3) to develop and calibrate a conceptual flow and transport model for the site and 4) to provide the opportunity to examine the effects of flow and geochemical transients on tracer transport.

**This project began in 2002. The first progress report is expected in late 2003.**

# Environmental Management Science Program Research in New Mexico

## Los Alamos National Laboratory

### 86680 – Ultra-Sensitive Elemental and Isotope Measurements with Compact Plasma Source Cavity Ring-Down Spectroscopy (CPS-CRDS)

**Principal Investigator:** Dr. Yixiang Duan

**Problem Area:** Subsurface Contamination

Development of robust and convenient instruments for trace-level actinide and hazardous elemental monitoring and analysis would be of significant benefit for many DOE applications. One significant need currently identified by DOE is the analysis of some alpha emitters (U, Pu, Am, etc.) in waste streams and groundwater. This is typically done with either ICP-MS or alpha scintillation counting (ASC). An ICP-MS can cost several hundred thousand dollars and cannot distinguish between isotopes with similar masses (i.e.,  $^{238}\text{Pu}$  and  $^{238}\text{U}$ ). ASC methods require tedious sample preparation and long time counting to detect isotopes with low energies.

We propose to explore ultrasensitive elemental and isotope measurements using cavity ring-down spectroscopy (CRDS) combined with a compact microwave plasma (CW) source as an atomic absorption cell. The research work will marry the high sensitivity of CRDS with a low power CW source to develop a new class of instrument that gives breakthrough sensitivity and capability for both elemental and isotope measurements. CRDS, which uses a single laser pulse ringing down inside the cavity over a thousand times, is 3 to 4 orders of magnitude more sensitive than conventional absorption techniques. Additional benefit is gained from a compact microwave plasma source that possesses advantages of low power, low plasma gas flow rate, and extended absorption path-length. All of these characteristics are favorable for atomic absorption measurement. A bench-type CRDS system will be upgraded and assembled with a tunable dye laser as the initial step for building a science base and producing raw data to demonstrate the feasibility of the new instrument. A compact microwave cavity will be designed to generate a linear plasma for sample atomization. Two sampling systems, for solution and gas respectively, will be built to introduce analytes into the plasma source. The ring-down signal will be monitored using a photomultiplier tube (PMT) and recorded using a digital oscilloscope interfaced to a computer. The project will start with common elements for initial experimental testing and instrument optimization. It will then switch to uranium isotopes (such as  $^{234}\text{U}$ ,  $^{235}\text{U}$ , and  $^{238}\text{U}$ ) and plutonium isotopes ( $^{238}\text{Pu}$  and  $^{239}\text{Pu}$ ). The proposed CW-CRDS technique will also be explored to resolve  $^{238}\text{U}$  and  $^{238}\text{Pu}$  isotopes, which are hardly resolved by ICP-MS due to isobaric interference. With these successful laboratory tests and solid base of data building, research efforts will then be made to develop field portable instrumentation for actinide isotope monitoring. Further work will focus on the construction of a small, portable CMP-CRDS unit using a diode laser. These small diode lasers are available for wavelengths ranging from the red through the near-infrared region and also over a narrow band in the blue region. The mounted diode lasers are at most only slightly larger than a typical helium-neon laser, yet possess an extremely narrow linewidth easily capable of isotopic resolution. The whole system can be designed in a compact way so that it can be easily used for field purpose. Since CRDS is capable of providing ultra-sensitive measurement of below  $10^{-6}$  fractional absorption, we expect the best detectivity of the CMT-CRDS system for elemental and isotopes to be around  $10^{-13}$ - $10^{-14}$  g/mi, which is orders of magnitude better than the values reported by ICP-MS. The breakthrough sensitivity and unique capability of the CW-CRDS could provide a powerful tool for DOE in diverse fields such as environmental remediation, long-term stewardship, waste management and characterization, decontamination and decommissioning, environmental monitoring, and other nuclear weapon related research. Using gas sampling, the technology could also be extended to offgas monitoring and worker exposure control. The proposed technology would offer capabilities that are not available in the current instruments. The proposed project will be jointly conducted in LANL, Mississippi State University, and Tiger Optics Inc.

**This project began in 2002. The first progress report is expected in late 2003.**

# **Environmental Management Science Program Research in New Mexico**

## **Los Alamos National Laboratory**

### **86687 – Phytosiderophore Effects on Subsurface Actinide Contaminants: Potential for Phytostabilization and Phytoextraction**

**Principal Investigator:** Dr. Christy Ruggiero

**Problem Area:** Subsurface Contamination

This proposal seeks to understand the influence of phytosiderophore-producing plants (grasses, including crops such as wheat and barley) on the biogeochemistry of actinide contaminants in the subsurface environment, and seeks to determine if these plants can be exploited for long-term contaminant stabilization or remediation. Grasses naturally produce phytosiderophores for solubilization, mobilization, and uptake of Fe and other essential mineral nutrients from soil. Similar chemical properties between Fe and Pu/Th suggest these natural chelators can be utilized to enhance removal of actinides from contaminated soils of stabilization of the actinides within the site. Numerous DOE sites contain Pu contamination which is of great concern due to possible contaminant mobility through wind, water, and other natural or man-made soil disturbances. There are no cost effective solutions currently available to stabilize or remediate these sites. We will demonstrate potential benefits of phytosiderophore-producing plants for long-term actinide contaminant stabilization by the plant's prevention of soil erosion and actinide migration through hydraulic control and/or through actinide removal through phytoextraction. We may also show possible harm caused by these plants through increased presence of actinide chelators that could increase actinide mobilization and migration in the subsurface environment. This information can then be directly applied by either removal of harmful plants, or be used to develop plant-based soil stabilization/remediation technologies. Phytoremediation (including both phytoextraction and phytostabilization) is a proven, viable commercial industry. Technology transfer to existing companies would be easy, and public perception and acceptance for these technologies is very high. A phytostabilization or phytoextraction system for actinide contamination could be the low cost, low risk, and acceptable technology needed for long-term stewardship of many DOE sites. Once we prove effectiveness, we envision an amazingly simple system for stewardship at actinide contaminated DOE sites: Where contamination is high enough to achieve cost effective extraction, we can plant a field of barley using low tillage techniques, plants remove Pu and other actinides from the soil, and then are harvested disposed. When contamination is lower, and therefore extraction is not cost effective, a slow growing perennial grass is planted which will slowly take up actinides and trap them in the plant rhizosphere and on the plant roots, thereby preventing both wind and water migration of the actinides.

**This project began in 2002. The first progress report is expected in late 2003.**

# Environmental Management Science Program Research in Washington

## Pacific Northwest National Laboratory

### 86729 – Mechanisms of CCl<sub>4</sub> Retention and Slow Release in Model Porous Solids and Sediments

**Principal Investigator:** Dr. Robert G. Riley

**Problem Area:** Subsurface Contamination

The transport and fate of non-polar hydrocarbons in soils and sediments depend in large part on the relative influence of sorptive and degradative processes. If the non-polar compound is not easily degraded, then, with time, diffusion into micropores, entrapment by internal cavities, and sorption to hydrophobic surfaces create a migration-resistant fraction (MRF). Although the diffusion/entrapment/sorption process has the positive attribute of retarding the transport of the non-polar compound, it also protects the compound from possible remediation by technologies based on rapid degradative processes. Eventually, the MRF serves as a slow-release source term once the original concentration gradient is reversed. Protection and slow release of contaminants by sediments frustrated many remediation attempts by significantly increasing the overall cost of cleanup and making it difficult to estimate natural attenuation rates.

The main objective of this project is to provide a better mechanistic description of the fundamental processes by which non-polar compounds are retained by sediments and subsequently released. We will focus our effort on the behavior of carbon tetrachloride (CCl<sub>4</sub>) in sediments, as CCl<sub>4</sub> is a contaminant of key concern at the Hanford Site and is not expected to degrade readily under the oxidizing conditions at the site. This objective will be reached through a combination of theory and experimentation with model systems and natural sediments.

Our unique approach encompasses three hypothesis-driven tasks. Task 1 will focus on sorption and release experiments with well-defined porous materials. An innovative system that circulates supercritical carbon dioxide will be used to artificially generate CCl<sub>4</sub> MRF in the porous media on a laboratory timescale. Assessment of the accumulation of the MRF and its slow-release behavior will be performed using a combination of analytical (gas chromatography, microbalance gravimetry) and spectroscopic (small-angle X-ray scattering, X-ray microscopy and tomography) measurements that will provide high-quality data about the spatial and temporal characteristics of the MRF. After the MRF behavior in the model porous media has been well defined, similar experiments will be conducted in Task 2 using natural sediment samples. Parallel release experiments will also be carried out using Hanford sediments that have been exposed to CCl<sub>4</sub> for several years. Task 3 will use a combination of lattice-Boltzmann simulations and continuum-based models to develop a coherent, mechanistic description of the overall entrapment and release process. Models will initially be developed for the well-defined porous materials and will later be applied to the more complex systems investigated in Task 2.

The success of the proposed work will provide the first mechanistic description of CCl<sub>4</sub> retention and release by porous materials and sediments and will represent a significant improvement in understanding the factors controlling these processes. Incorporation of this information into numerical transport models will improve predictive accuracy and robustness. Moreover, the enhanced predictive capability arising from the proposed work is expected to have a large impact on current deliberations regarding active remediation versus monitored natural attenuation of the extensive CCl<sub>4</sub> plume at the Hanford Site. Ready extension of this knowledge to other chlorinated hydrocarbon compounds contaminating Department of Energy sites as well as other organic contaminants would be expected.

**This project began in 2002. The first progress report is expected in late 2003.**



# **Environmental Management Science Program Research in Washington**

## **Pacific Northwest National Laboratory**

### **86736 – Armored Enzyme Nanoparticles for Remediation of Subsurface Contaminants**

**Principal Investigator:** Dr. Jay W. Grate

**Problem Area:** Subsurface Contamination

We propose a research program in the synthesis and characterization of armored enzyme nanoparticles that dramatically stabilize the activity of the enzyme. Stabilization of enzyme activity is a critical advance that is required in order to use enzymes effectively for the remediation of organic compounds in soil or water. The structures of these nanoparticles contain a single enzyme in the center with a porous composite organic/inorganic shell on the outside. Hence, these are nano-bio-composites. The synthesis and properties of these nanoparticles will be investigated and characterized in detail, beginning with a protease ( $\alpha$ -chymotrypsin) and tyrosinase, both of which are commercially available. We will also clone and engineer a haloalkane dehalogenase for the degradation of trichloroethylene (TCE) and other chlorinated hydrocarbons of interest to DOE. This enzyme is a broad specificity hydrolase requiring no cofactors that is active in the presence or absence of oxygen. We will then create armored enzyme nanoparticles from the engineered dehalogenase to create armored dehalogenase nanoparticles with exceptional stability.

**This project began in 2002. The first progress report is expected in late 2003.**

# Environmental Management Science Program Research in Washington

## Pacific Northwest National Laboratory

### 86740 - Phosphate Barriers for Immobilization of Uranium Plumes

**Principal Investigator:** Dr. Johnathan P. Icenhower

**Problem Area:** Subsurface Contamination

At least seven distinct uranium-contaminated plumes have been identified at the Hanford site, Washington State, yet conventional remediation strategies, such as pump and treat, are expensive and have not diminished the concentration of uranium. Previous attempts to employ a phosphate remediation strategy have failed because: 1) the selected forms of soluble phosphate rapidly generate precipitates that plug the well near the point of injection, and 2) uncertainty concerning the longevity of the phosphate barrier effectiveness. Longevity of phosphate barriers cannot be assessed because solubilities of key uranyl phosphate minerals (autunite and meta-autunite) are poorly understood; a 25 order of magnitude difference in log  $K_{sp}$  values are reported for autunite.

Our hypothesis is that long-chain polyphosphate compounds can provide the necessary control over the precipitation kinetics of insoluble phosphates so that injection, mixing, and immobilization of the uranium can be effectively accomplished in the subsurface. For the first time, we propose to monitor the hydrolyzation kinetics of sodium polyphosphate and precipitation of autunite minerals in a porous medium under *in-situ* conditions of partial hydraulic saturation. A unique combination of equipment available only at PNNL will be used for these experiments that includes the patented Pressurized Unsaturated Flow (PUF) system, linked with a scanning Laser Raman Spectrometer and X-ray Microfocus Tomograph (XMT). Interpretation of these experiments will be aided by independent solubility studies on autunite and meta-autunite. Isopiestic methods will be used to perform the measurements over a range of water activity; uranyl phosphate minerals are subject to dehydration reactions upon exposure to humid air that significantly affects their structure and, we believe, their aqueous solubility. NMR and laser-induced photoacoustic spectroscopy will be used to determine speciation of uranyl and phosphate in solution. These data will lay a solid scientific foundation for an alternative remediation method for uranium plumes that can be *effectively* deployed in the field.

**This project began in 2002. The first progress report is expected in late 2003.**

# **Environmental Management Science Program Research in Washington**

## **Pacific Northwest National Laboratory**

### **86748 - Characterization of U(VI) Sorption-Desorption Processes and Model Upscaling**

**Principal Investigator:** Dr. John M. Zachara

**Problem Area:** Subsurface Contamination

Uranium (VI) is a common subsurface contaminant on DOE lands because of its central role in the nuclear fuel cycle. U(VI) groundwater plumes exist at Hanford, Oak Ridge, Savannah River, and other DOE sites. At each of these locations, DOE, regulators, and stakeholders are attempting to identify the best corrective and remedial actions for these U(VI)-plumes to protect human health and valuable environmental resources. Typically, the credibility of such assessments has been low because of inability to forecast in-ground U(VI) migration rates and redistribution. An insufficient scientific understanding of U(VI) geochemistry, and lack of knowledge of the various mineralogic, geochemical, geophysical factors that control the rates and extent of U(VI) reactions in commonly heterogeneous subsurface environments are key impediments. In this proposal we plan to characterize sorption and desorption processes of U(VI) on pristine and contaminated Hanford sediments over a range of sediment facies and materials properties. The sediments will be obtained from vertical cores collected from outside and inside waste sites, and will include the important geologic formations and facies types in which U(VI) contaminant plumes exist. The physical and chemical properties of the sediments will be incrementally characterized with increasing sophistication until controlling properties are identified. Molecular speciation measurements of adsorbed and precipitated U(VI) will be made using X-ray absorption and laser induced fluorescence spectroscopy with the objective of developing speciation-based conceptual and numeric models of sorption/desorption. The implications of intragrain mass transfer and reaction will be investigated using U- spiked/contaminated materials varying in U-contact time up to 30 years or more. Geochemical and mass transfer model parameters will be correlated with sediment physical, chemical, and mineralogic properties in attempt to develop a site-wide model for U(VI) geochemical retardation. Simple, volume-based upscaling relationships will be established for both sorption and desorption processes. The developed models and upscaling relationships will be tested at a U(VI) vadose zone field injection experiment to be performed by others where sediment geochemical/geophysical properties and U-plume evolution can be sampled and studied at scales ranging from centimeters to tens of meters. The research will provide new insights on the mechanisms of U(VI) retardation at Hanford and approaches to upscale laboratory developed geochemical models for defensible field-scale predictions.

**This project began in 2002. The first progress report is expected in late 2003.**

# **Environmental Management Science Program Research in Washington**

## **Pacific Northwest National Laboratory**

### **86753 - The Aqueous Thermodynamics and Complexation Reactions of Anionic Silica and Uranium Species to High Concentration**

**Principal Investigator:** Dr. Andrew R. Felmy

**Problem Area:** Subsurface Contamination

High ionic strength, highly basic tank wastes containing several important radionuclides, including  $^{90}\text{Sr}$ ,  $^{99}\text{Tc}$ , and  $^{60}\text{Co}$ , as well as actinide elements (isotopes of U, Pu, and Am) are known to have leaked into the vadose zone at the Hanford Site. Determining the magnitude of these tank leaks, the extent of migration of the radionuclides, and their potential future mobility are some of the most daunting challenges facing Hanford and other DOE sites.

Anionic silica species can represent a primary transport vector for radionuclides in the subsurface owing to the dissolution of silica and aluminosilicate minerals upon interactions with the basic Hanford tank wastes. In order to address these issues, we have developed the first reliable high ionic strength thermodynamic model for polysilicate species (including monomers, dimers, trimers, ...) at 25°C, evaluated the effects of these silicate species on Sr solubility, complexation, and potential mobility, developed new stability constants for Sr, Co(II), U(VI), and Am(III) silica complexes, developed a molecular model for determining the protonation state and structure of these complexes, developed initial data on Cm(III) polysilicate complexation and polysilicate anion interactions, and discovered previously unidentified enantiomeric forms of polysilicates species. In addition, we have provided computer code and a new thermodynamic database for modeling high ionic strength solutions to scientists working on the Hanford Groundwater/Vadose Zone Integration Project (IP). In this follow-on project, we propose to complete the studies on silica complexation, expand our efforts to address other key thermodynamic data needs related to U(VI) complexation at the Hanford Site, and continue our collaboration with members of the IP program.

**This project began in 2002. The first progress report is expected in late 2003.**

# **Environmental Management Science Program Research in Washington**

## **Pacific Northwest National Laboratory**

### **86759 - Radionuclide Sensors for Water Monitoring**

**Principal Investigator:** Dr. Jay W. Grate

**Problem Area:** Subsurface Contamination

We propose to renew a research program directed toward developing novel sensor concepts and materials for sensitive and selective determination of beta- and alpha-emitting radionuclide contaminants in water. We have developed preconcentrating radionuclide sensors capable of detecting radionuclides to regulatory levels such as drinking water standards. In order to meet the requirements for isotope specific detection at ultra-low regulatory levels the proposed sensors are based on radiometric detection. In order to address the fundamental challenge of short ranges of beta and alpha particles in water, our overall approach is based on localization of preconcentration/separation chemistries directly on or within the active area of a radioactivity detector. Radionuclides of primary interest for DOE needs are alpha- and beta- emitting radionuclides that are mobile in the environment, including Sr-90, Tc-99, and actinides.

The outcome of these investigations will be the knowledge necessary to choose appropriate chemistries for preconcentration of radionuclides with selectivity over other matrix components and interferences, novel preconcentrating column sensors, and improved instrumentation and signal processing for selective radionuclide sensors. New knowledge of the performance of sensing materials, sensor configurations, and quantitative analytical approaches will provide the basis for designing effective probes and instrumentation for field analytical chemistry and *in situ* sensing.

**This project began in 2002. The first progress report is expected in late 2003.**

# Environmental Management Science Program Research in Michigan

## University of Michigan

### 86797 - Engineered Natural Geosorbents for In-Situ Immobilization of DNAPLs and Heavy Metals

**Principal Investigator:** Dr. Walter J. Weber, Jr.

**Problem Area:** Subsurface Contamination

Extensive subsurface contamination by dense non-aqueous phase liquid (DNAPL) organic solvents and heavy metals is commonplace at many DOE facilities. Poor performances and excessive costs have made traditional technologies and approaches less than satisfactory for remediation of such sites. It is increasingly apparent that marginal improvements in conventional methods and approaches will not suffice. Innovative approaches using new and/or existing technologies in more efficient and cost-effective ways are thus urgently required. The in-situ irreversible immobilization and inactivation concept proposed herein is one such innovative approach. The concept is predicated on the hypothesis that it is possible to employ indigenous natural geosorbents, either as they exist or as appropriately modified, to bind and sequester chlorinated organic solvents and heavy metals irreversibly, and thus eliminate or greatly reduce their associated environmental risks. The technologies that can be brought to bear on the implementation of this concept are for the most part readily available, but in neither organized form nor optimized state. The research described here addresses both of these deficiencies. Common components of DNAPLs and most heavy metals are known to be sorbed by the natural organic matter, mineral, and/or clay components of typical soils and sediments. It is also known that the specific physicochemical properties of these geosorbents significantly affect the strengths and extents of their respective sorption reactions with different organic and inorganic contaminants. The more aromatic and chemically condensed (hard carbon) forms of soil/sediment organic matter (SOM) have much higher and less reversible sorption capacities for organic chemicals and heavy metals than do the more aliphatic and highly amorphous (soft carbon) forms of SOM. The sorption properties of SOM matrices are thus directly related to the degree of geochemical diagenesis they have undergone. We have recently demonstrated that the sorption energies and capacities of SOM matrices for organic chemicals can be greatly increased by treatment with superheated water to simulate and accelerate geochemical diagenesis. The sorption capacities of many other naturally occurring materials (e.g., bark, peanut husk, peat, bentonite, and zeolites, etc.) for heavy metals also have been shown to be improved by thermal treatment. The overarching goal of the proposed research is to develop a comprehensive data and knowledge base with respect to the mechanisms of binding and sequestration of DNAPL components and heavy metals by different types of soil matrices. Our ultimate objective is the application of this knowledge and information base as a platform for designing specifically engineered geosorbents capable of in-situ long-term immobilization and inactivation of non-aqueous phase organic liquids and heavy metals at contaminated DOE sites and facilities. The engineered geosorbents will be developed using soils indigenous to each study site, modified as necessary to impart a prescribed set of sequestration properties. Such modifications will in some cases involve treatments to change the inherent properties of the native soil matrices, and in some cases the addition of other low-cost and readily available natural materials. The end product of the proposed research efforts will be a suite of cost-effective media that can be prepared and applied on-site to immobilize and inactivate DNAPL and heavy metal contaminants. The research we propose will substantially enrich our understanding of the environmental fate and risks of DNAPLs and heavy metals at DOE facilities and sites. A new technology we have developed to measure long-term potentials for release of soil-associated contaminants will facilitate our initial characterizations of selected DOE sites and subsequent ongoing monitoring programs for these and other sites. Such data will be invaluable in determinations of the probable effectiveness of alternative management strategies. The engineered geosorbents to be developed will provide highly flexible and cost-effective materials that can be applied in appropriate configurations (e.g., permeable barriers, slurry walls, tilling into surface soils, etc.) to arrest migration of contaminants of concern and eliminate their potentially harmful environmental effects.

**This project began in 2002. The first progress report is expected in late 2003.**

# Environmental Management Science Program Research in Minnesota

## University of Minnesota

### 86800 - Reactive Membrane Barriers for Containment of Subsurface Contamination

**Principal Investigator:** Dr. William A. Arnold

**Problem Area:** Subsurface Contamination

The treatment or remediation of contaminants at some sites is neither technically nor economically feasible. Containment or stabilization of these subsurface contaminants, therefore, may be the only viable alternative for the protection of human and ecological health. The overall goal of the proposed research is the development of reactive membrane barriers. These membranes are a powerful, novel, and versatile technique to contain and stabilize subsurface contaminants. These membrane barriers will be used to prevent the migration of organic and inorganic contaminants in both the vadose and saturated zones and will also be able to prevent the transport of non-aqueous phase liquids (NAPLs) from source zones.

This work will focus on reactive membrane barriers containing either zero-valent iron (Fe(0)) particles or crystalline silicotitanate (CST) particles. The use of geomembranes comprised of polymers to contain or stabilize contamination is based on drastically slowing the diffusion of contaminants into uncontaminated areas by creating a barrier using the membrane material. Diffusion through the membrane barrier is slow, but contaminants will eventually break through. The time to breakthrough can be increased and the diffusion process itself can be slowed through the use of reactive membrane barriers. Reactive particles serve to either immobilize or transform contaminants within the membrane, and thus increase the time to breakthrough. Membranes containing clay(mica) flakes further increase the diffusion path length and decrease the permeability of the polymer material. It is anticipated that inclusion of reactive particles in membrane barriers will prevent contaminant breakthrough 100-1000 times longer than the polymer alone. An additional factor of 10 will be gained by the addition of inert flakes. These reactive membranes represent a potential major advance in subsurface contaminant containment.

The specific objectives of this project are to manufacture, test, and model the performance of the reactive membrane barriers described above. Specific tasks are to:

1. Manufacture and test polyvinyl alcohol (PVA) membranes containing reactive particles with and without inert particles/flakes.
2. Manufacture and test high-density polyethylene (HDPE) membranes containing reactive particles with and without inert particles/flakes.
3. Test the performance of the membranes with groundwater collected from one or more DOE sites to determine whether interference by components in the groundwater matrix in occurs.
4. Use mathematical and/or numerical models to develop a set of analytical guidelines that facilitate the development of reactive barrier films to allow their application at contaminated DOE sites.

**This project began in 2002. The first progress report is expected in late 2003.**

# **Environmental Management Science Program Research in Idaho**

## **Idaho National Engineering and Environmental Laboratory**

### **86803 - Underground Corrosion after 32 Years: A Study of Fate and Transport**

**Principal Investigator:** Dr. Kay Adler Flitton

**Problem Area:** Subsurface Contamination

In 1970, the National Institute of Standards and Technology (NIST) implemented the most ambitious and comprehensive long-term corrosion behavior test to date for stainless steels in soil environments. Thirty-two years have passed since scientists buried 6,324 specimens from stainless steel types, specialty alloys, composite configurations, and multiple material forms and treatment conditions at six distinctive soil-type sites throughout the country. Today, there are more than 190 specimens per site, exceeding a total of 1000 specimens that remain undisturbed, a buried treasure of subsurface scientific data.

This proposal advocates a similarly ambitious research project that completes the NIST corrosion study and thoroughly examines the soil and environment surrounding the specimens. The project takes an interdisciplinary research approach that will correlate the complicated interrelationships among metal integrity, corrosion rates, corrosion mechanisms, soil properties, soil microbiology, plant and animal interaction with corrosion products, and fate and transport of metallic ions. The results will provide much needed data on corrosion rates, underground material degradation, and the behavior of corrosion products in the near-field vadose zone. The data will improve the ability to predict the fate and transport of chemical and radiological contaminants at sites throughout the DOE complex.

This project specifically addresses the EMSP solicitation (LAB-02-03) call for research related to subsurface contamination and transport processes in the vadose and saturated zones. This research opportunity also directly applies to environmental management operational corrosion issues, and long-term stewardship scientific needs for understanding the behavior of waste forms and their near-field contaminant transport.

**This project began in 2002. The first progress report is expected in late 2003.**



# **Environmental Management Science Program Research in Idaho**

## **Idaho National Engineering and Environmental Laboratory**

### **86804 - Resolving the Impact of Biological Processes on DNAPL Transport in Unsaturated Porous Media through Nuclear Magnetic Resonance Relaxation Time Measurements**

**Principal Investigator:** Dr. Russel Hertzog

**Problem Area:** Subsurface Contamination

Knowing how environmental properties affect dense non-aqueous phase liquid (DNAPL) solvent flow in the subsurface is essential for developing models of flow and transport in the vadose zone that are needed for designing remediation and long-term stewardship strategies. For example, one must know if solvents are flowing in water-wet or solvent-wet environments, the pore-size distribution of the region containing DNAPLs, and the understanding of how physical and biological properties of porous media influence water and DNAPL distribution under saturated and unsaturated conditions. This project investigates the capability and limitations of low-field nuclear magnetic resonance (NMR) relaxation decay-rate measurements for determining environmental properties affecting DNAPL solvent flow in the subsurface. The oil and gas industry uses NMR measurements in deep subsurface formations to determine porosity and hydrocarbon content and to estimate formation permeability. These determinations rely on NMR's ability to distinguish between water and hydrocarbons in the pore space and to obtain the distribution of pores sizes from relaxation decay-rate distributions. The potential of NMR decay rate distributions for characterizing DNAPL fluids in the subsurface and understanding their flow mechanisms has not been exploited. Near-surface unsaturated vadose zone environments provide unique challenges for using NMR. These challenges will be addressed through systematic laboratory experiments and a program of research to extend and adapt current field NMR measurements to near-surface environmental problems.

**This project began in 2002. The first progress report is expected in late 2003.**

# **Environmental Management Science Program Research in Idaho**

## **Idaho National Engineering and Environmental Laboratory**

### **86805 - Coupling of Realistic Rate Estimates with Genomics for Assessing Contaminant Attenuation and Long-Term Plume Containment**

**Principal Investigator:** Dr. Frederick S. Colwell

**Problem Area:** Subsurface Contamination

Dissolved dense non-aqueous phase liquid plumes are persistent, widespread problems in the DOE complex. While perceived as being difficult to degrade, at the Idaho National Engineering and Environmental Laboratory, dissolved trichloroethylene (TCE) is disappearing by natural attenuation, a finding that saves significant site restoration costs. Acceptance of monitored natural attenuation as a preferred treatment technology requires direct proof of the process and rate of the degradation. Our proposal aims to provide that proof for one such site by testing two hypotheses. First, we believe that realistic values for in-situ rates of TCE cometabolism can be obtained by sustaining the putative microorganisms at the low catabolic activities consistent with aquifer conditions. Second, the patterns of functional gene expression evident in these communities under starvation conditions while carrying out TCE cometabolism can be used to diagnose the cometabolic activity in the aquifer itself. Using the cometabolism rate parameters derived in low-growth bioreactors, we will complete the models that predict the time until background levels of TCE are attained at this location and validate the long-term stewardship of this plume. Realistic terms for cometabolism of TCE will provide marked improvements in DOE's ability to predict and monitor natural attenuation of chlorinated organics at other sites, increase the acceptability of this solution, and provide significant economic and health benefits through this noninvasive remediation strategy. Finally, this project will derive valuable genomic information about the functional attributes of subsurface microbial communities upon which DOE must depend to resolve some of its most difficult contamination issues.

**This project began in 2002. The first progress report is expected in late 2003.**

# Environmental Management Science Program Research in Idaho

## Idaho National Engineering and Environmental Laboratory

### 86807 - Long-Term Stewardship of Mixed Wastes: Passive Reactive Barriers for Simultaneous In Situ Remediation of Chlorinated Solvent, Heavy Metal, and Radionuclide Contaminants

**Principal Investigator:** Dr. William Apel

**Problem Area:** Subsurface Contamination

A survey of 18 DOE sites showed 11 to have groundwater contaminated by radionuclide, heavy metal, and halocarbon mixtures. New, effective, economical cleanup technologies are needed to remediate these sites. We advocate developing such a technology for *in situ* halocarbon degradation and simultaneous radionuclide/heavy metal immobilization in groundwater using passive reactive barriers (PRBs) formed with bacteria from the genus *Cellulomonas*. We recently discovered these bacteria in the U.S. DOE Hanford site subsurface, and found they can catalyze dissimilatory metal and radionuclide reduction (e.g. iron, chromium, uranium). Uranium and chromium reduction results in decreased solubility/immobilization. Reduced iron can catalyze halocarbon degradation, so *Cellulomonas* can potentially degrade halocarbons via iron reduction. Furthermore, *Cellulomonas* can reduce metals/radionuclides using inexpensive carbon sources, with reduction continuing for prolonged periods after carbon source depletion. We propose conducting the research necessary to develop PRBs with *Cellulomonas* by testing the following hypotheses:

- A wide spectrum of electron donors and acceptors will allow simultaneous treatment of groundwater contaminated with mixtures of halocarbons, radionuclides, and heavy metals.
- Indigenous *Cellulomonas spp.* can provide long-term activity as the active component of PRBs even in the absence of carbon sources.
- *Cellulomonas spp.* are present at numerous DOE subsurface sites and represent a metabolically important group influencing the fate of reducible groundwater contaminants.
- The choice of electron donor and development of effective substrate addition strategies will allow establishment and control of sessile *Cellulomonas* communities to form effective PRBs that will degrade halocarbons and immobilize heavy metals and radionuclides.

**This project began in 2002. The first progress report is expected in late 2003.**

# Environmental Management Science Program Research in Washington

## Washington State University

### 86814 - Colloid-Facilitated Transport of Radionuclides Through the Vadose Zone

**Principal Investigator:** Dr. Markus Flury

**Problem Area:** Subsurface Contamination

Radioactive and hazardous wastes stored in the underground tanks at the Hanford site have leaked into the vadose zone. Many of these waste streams were highly caustic. Waste sediment interaction has resulted in a wide array of dissolution and precipitation reactions, resulting in secondary solids that have sorbed or coprecipitated with contaminants. Characterization activities in the tank farms have clearly shown that the waste plumes are being driven to depth in the vadose zone by the infiltration of low-ionic strength meteoric waters and the leakage of dilute Columbia River water from ubiquitous process-water supply lines. This scenario of concentrated, reactive waste, followed by low ionic strength water, encourages colloid mobilization. Other, less electrolyte- concentrated waste streams, like cribs and French drains, are also conducive to *in situ* colloid mobilization, when meteoric water dilutes and displaces the waste plumes. The goal of this project is to elucidate the role, and quantify the relevance, of colloids in facilitating the transport of contaminants in the Hanford vadose zone. We will focus on (1) thermodynamic stability and mobility of colloids formed by reactions of sediments with highly alkaline tank waste solutions, (2) colloid-contaminant interactions, and (3) *in situ* colloid mobilization and colloid-facilitated contaminant transport occurring in both contaminated and uncontaminated Hanford sediments. As contaminants to study colloid-facilitated transport, we have selected Cs, Eu, and Am. We will consider two different types of colloids that can potentially facilitate the movement of radionuclides: newly formed colloidal materials due to reactions of tank waste with subsurface sediments, and native colloidal material present in the sediments. The newly formed colloidal phases, identified as zeolites and feldspathoids, may not be stable when geochemical conditions change at which they were formed. We will determine the thermodynamic stability of the zeolites and feldspathoids under conditions representative for the Hanford subsurface. The interactions of Cs, Eu, and Am with newly-formed and native colloidal particles isolated from the sediments will be investigated with batch sorption and spectroscopic techniques. In column tests using representative sediment samples from the Hanford site, we will examine the potential for *in situ* mobilization of colloids. Waste plume displacement by typical meteoric and pore water will be simulated in packed columns as well as in undisturbed soil monoliths. Experiments will be carried out under variably saturated, steady-state and transient water flow to study the effect of water content and flow-interruptions on colloid mobilization and transport. We will use X-ray tomography and NMR to visualize colloidal movement in the porous media. We will also study colloid mobilization from selected contaminated sediment samples from the Hanford site. Thermodynamic stability, sorption, and column studies will be analyzed with a two-phase reactive transport model in which relevant processes for colloid-facilitated transport of radionuclides will be incorporated. The results of the proposed research will lead to a better understanding of colloid-formation, colloid-contaminant-soil interactions, colloid migration, and colloid-facilitated transport in the vadose zone. The experiments proposed here use conditions specific to various waste streams at the Hanford site, and the results are therefore directly applicable to clean-up strategies and procedures for Hanford contamination problems. We will provide conclusive evidence under what conditions colloid-facilitated transport can be expected at the Hanford site, and what the quantitative magnitude of this transport process will be.

**This project began in 2002. The first progress report is expected in late 2003.**

# Environmental Management Science Program Research in Oregon

## Oregon Health & Science University

### 86820 - Overcoming Barriers to the Remediation of Carbon Tetrachloride Through Manipulation of Competing Reaction Mechanisms

**Principal Investigator:** Dr. Paul G. Tratnyek

**Problem Area:** Subsurface Contamination

Most approaches that have been proposed for the remediation of groundwater contaminated with carbon tetrachloride ( $\text{CCl}_4$ ) produce chloroform ( $\text{CHCl}_3$ ) as the major product and methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) as a minor product. Both of these products are nearly as persistent and problematic as the parent compound, but competing reaction pathways produce the more desirable products carbon monoxide (CO) and/or formate ( $\text{HCOO}^-$ ). Results scattered throughout the chemical and environmental engineering literature show that the branching between these reaction pathways is highly variable, but the controlling factors have not been identified. If we understood the fundamental chemistry that controls the branching among these, and related, product-formation pathways, we could improve the applicability of a host of remediation technologies (both chemical and biological) to the large plumes of  $\text{CCl}_4$  that contaminate DOE sites across the country. This project will provide the first complete characterization of the mechanisms and kinetics of competing degradation reactions of  $\text{CCl}_4$  through laboratory experiments in simple model systems closely coordinated with theoretical modeling studies. The results provide strategies for maximizing the yield of desirable products from  $\text{CCl}_4$  degradation, and the most promising of these will be tested in column model systems using real site waters and matrix materials.

**This project began in 2002. The first progress report is expected in late 2003.**

# Environmental Management Science Program Research in South Carolina

## Savannah River Ecology Laboratory

### 86845 - Linking Chemical Speciations, Desorption Kinetics, and Bioavailability of U and Ni in Aged-Contaminated Sediments: A Scientific Basis for Natural Attenuation and Risk Assessment

**Principal Investigator:** Dr. Paul M. Bertsch

**Problem Area:** Subsurface Contamination

The extent to which heavy metals and radionuclides pose an environmental hazard depends on their potential for release to and transport in the environment, i.e., environmental availability, and their potential for introduction into biological systems, i.e., bioavailability. Although there exists a substantial body of literature pertaining to the fate, distribution, and bioavailability of contaminant metals in model laboratory systems, few studies have examined the biogeochemical cycling of heavy metals in complex aged contaminated soils and sediments at a fundamental level. Even fewer have coupled detailed information on chemical speciation from state-of-the-art microscopic analytical and spectroscopic techniques with macroscopic observations obtained using indirect chemical extractions, metal desorption and leaching experiments, and biological uptake and toxicity assays.

Consequently, a major knowledge gap exists in translating basic geochemical science performed in simple model systems, short duration sorption/desorption laboratory experiments, and decoupled aqueous and solid phase speciation studies to real world systems that reflect the complexity arising from interaction of mixed waste contaminant source terms, long term aging reactions, multiple mineral surfaces, and naturally occurring organic matter. Moreover, the fundamental reactions governing contaminant aging, environmental availability, and bioavailability of metals and radionuclides, which dramatically influence the efficacy of environmental remediation and management strategies, remain poorly defined and understood.

The overall goal of this project is to address these fundamental knowledge gaps by investigating specific aging mechanisms for U and Ni released to the Savannah River Site environment from a compositionally and temporally defined source term and aged in dynamic riparian/wetland sediments for over 30 years. Knowledge about the timing and composition of past contaminant discharges coupled with the unique sediment stratification present at the study site provides a tremendous opportunity to examine the relative role(s) of reactive mineral and organic phases in metal sequestration processes. The proposed research represents a unique opportunity to establish clear linkages between aging, soil/sediments properties, chemical speciation, environmental availability, and bioavailability of U and Ni.

We propose a novel coupling of (1) wet chemical (indirect) and advanced spectroscopic (direct) speciation techniques, (2) aqueous and solid phase speciation and bioavailability assays, (3) macroscopic observations from desorption and leaching experiments and microscopic level information on molecular contaminant speciation and sediment properties to address the following hypotheses: **Hypothesis I.** Aging of U and Ni contaminated sediments results in redistribution of U and Ni into less labile, less bioavailable forms and associations with sediment Fe-oxides and organic matter; **Hypothesis II.** A clear relationship exists between chemical speciation, key sediment properties, and sorption/desorption processes of U and Ni in sediments; **Hypothesis III.** A clear relationship also exists between chemical speciation and simple biological metrics of uptake and toxicity assays.

These linkages are essential for developing rational and scientifically sound risk assessment methods, evaluating the potential of natural attenuation processes and engineered remediation strategies for reducing metal toxicity and human and ecological risk, and for understanding the fundamental processes governing cycling of heavy metals and radionuclides in the environments. This research will also provide a context in

which to understand how results from indirect and direct chemical speciation techniques and bioavailability assays relate to the complexity of contaminated soil and sediment systems encountered in the field.

**This project began in 2002. The first progress report is expected in late 2003.**

# **Environmental Management Science Program Research in Georgia**

## **Georgia Institute of Technology**

### **86870 - Differential Group-Velocity Detection of Fluid Paths**

**Principal Investigator:** Dr. Timothy L. Long

**Problem Area:** Subsurface Contamination

This proposal is to develop and test a new technology to aid in the selection and design of remediation options in shallow aquifers. The objective of the technology is to map the primary fluid pathways in shallow soils. We propose to measure perturbations in the shear wave velocity of the soil by measuring changes in seismic response either induced by natural processes, (e.g. rainfall) or induced actively by pumping and withdrawal of fluids. The observed changes in surface-wave velocity will then be used to map areas where fluids modified the fluid pressure and, hence, the shear-wave velocity. The proposed technique should identify areas reached by the fluids under normal or induced flow patterns. The proposed technique takes advantage of the abilities of signal-processing techniques to detect small differences in propagation. The differences will indicate flow paths relative to a reference structure that need only approximate the actual structure. In effect, we propose an inversion of the perturbation of surface wave velocity instead of the inversion of surface wave dispersion for structure.

We demonstrate in this proposal that perturbations in phase velocity can be measured in detail by computing the Fourier transform of the difference of normalized traces. We expect the differential measurements to provide significantly better precision than is possible with the direct estimation of the structure from a dispersion curve. We propose during the first year to test the data reduction techniques on theoretical and field data. During the second year we propose to carry out one or more field tests of the technique.

The perturbations in the velocity structure will indicate where, in a time sequence, the pumped fluids have influenced the shear-wave velocity. Areas experiencing the greatest pressure and material properties changes would indicate primary flow paths and zones that are most likely amenable to remediation by extraction or flushing. A time sequence of tests could monitor the dispersion and movement of the induced perturbations. The technique could be used prior to remediation to detect flow paths and, hence, help design an optimal remediation process. It could be used during remediation to detect and determine which zones are reached by the remediation.

**This project began in 2002. The first progress report is expected in late 2003.**



# Environmental Management Science Program Research in Wisconsin

## University of Wisconsin at Madison

### 86890 - A Resolution Analysis of Two Geophysical Imaging Methods for Characterizing and Monitoring Hydrologic Conditions in the Vadose Zone

**Principal Investigator:** Dr. David L. Alumbaugh

**Problem Area:** Subsurface Contamination

Geophysical methods are rapidly becoming popular within the DOE complex as possible tools for characterizing subsurface hydrologic properties, as well as monitoring flow and transport processes within the vadose zone at contaminated sites. **The reason for incorporation geophysical imaging into site characterization, remediation monitoring, or as a long term monitoring tool for a site closure plan is simple; these methods offer the possibility to non-destructively characterize subsurface conditions and processes from a limited number of boreholes and/or measurements made on the surface.** To convert between geophysical and hydrological properties requires the application of petrophysical models. In general petrophysical models are approximate, empirical relations developed from the studies of core-sized (a few cm) samples. However, geophysical images typically have resolutions on the order of fractions of meters or larger. In the past, there has been little work done to quantify the effect of heterogeneity due to structures that are larger than core samples but still too small to be resolved individually by geophysical imaging. In addition there has been little work done to quantify the resolution of the imaging schemes that addresses their ability to characterize spatial heterogeneity within the vadose zone, and produce accurate time-lapse images of flow and transport processes. The effects of data error on the images such as sensor work it is important to consider the cumulative effect of errors in both the geophysical data collection and processing, and within petrophysical models themselves, if interpreters are to understand those features in the images that are real, those that are artifacts, and how much credence can be given to the results in terms accuracy and precision.

We propose an intensive numerical modeling effort that is aimed at helping to resolve some of these issues for the electrical resistivity tomography (ERT) and crossborehole ground penetrating radar (XBGPR) geophysical methods as applied to characterizing and monitoring vadose zone properties and processes. The proposed research will consist of four primary tasks; 1) high definition, large-scale numerical modeling of a series of statistically related vadose zone flow and transport processes to yield porosity, moisture content, temperature, and solute concentrations at 5 to 10cm intervals throughout a 1000 to 4000 m<sup>3</sup> volume hypothetical vadose zone; 2) application and analysis of petrophysical relationships that convert the output of the hydrologic models from task 1 into geophysical parameter fields; 3) generation of synthetic ERT and XBGPR data sets from the geophysical parameter fields generated in task 2, and addition of random measurement noise and biased error to the data; and 4) imaging of the synthetic data sets using standard geophysical processing and inversion techniques, and comparison of the results to the original hydrologic models. The results of this effort will not only be employed to analyze the resolution and accuracy of the two geophysical methods for imaging within the vadose zone, but also will be applied to better understand data collected during a series of vadose zone flow and transport experiments that have been conducted at the Sandia-Tech Vadose Zone (STVZ) experimental facility in Socorro, New Mexico, over the last four years. The benefits to the DOE's Environmental Management Program include a thorough evaluation of how well two the geophysical imaging methods (i.e., ERT and XBGPR) can truly resolve subsurface hydrological features and processes within the vadose zone, synthetic data sets for other researchers to use for testing and assessment and an assessment of an interactive method for determining subsurface flow and transport properties within the vadose zone. The team of scientists from Sandia National Laboratories, the University of Wisconsin-Madison, and multiphase Technologies, LLC, brings a unique perspective to the project combining expertise in vadose zone hydrology, numerical modeling, and geophysical imaging.

**This project began in 2002. The first progress report is expected in late 2003.**

# Environmental Management Science Program Research in Washington

## University of Illinois at Chicago

### 86898 - Reactivity of Primary Soil Minerals and Secondary Precipitates Beneath Leaking Hanford Waste Tanks

**Principal Investigator:** Dr. Kathryn L. Nagy

**Problem Area:** Subsurface Contamination

Since the late 1950s, leaks from 67 single-shell tanks at the Hanford Site have been detected or suspected, resulting in the release of about 1 million curies to the underlying sediments. The Hanford Tri-Party Agreement calls for the initiation of remediation at the 200 Area tank farms in 2004. There is a risk that these activities may add to and/or mobilize the existing inventory of contaminants in the vadose zone. At issue is the distribution of contaminants beneath the tanks, the processes that led to their current disposition and the processes that will control their future mobility. The high ionic strength, high pH, and high aluminum concentrations in the tank liquids can significantly alter the vadose zone sediments through dissolution of primary minerals and precipitation of secondary minerals. These processes directly influence (1) the flow paths that control contaminant transport and (2) the reactivity of the solid matrix that controls contaminant mobility. Scientifically defensible decisions on tank remediation must consider the impact of these physical and geochemical processes. However, fundamental knowledge is lacking on the mineral reaction kinetics and the dynamic interaction of the reactions with the flow field and contaminant sorption.

We propose to address three specific issues with respect to obtaining accurate rate laws and quantifying radionuclide uptake in systems representing waste fluids from tanks and other disposal sites at Hanford, Washington and minerals in Hanford sediments. The first two issues will build on the results obtained in a previously funded EMSP project (70070). First, we will continue to quantify rates for selected sediment minerals as a function of recognized factors that control the kinetics of dissolution and precipitation in the unnatural system of waste solutions mixing with soils. These include the effect of high pH, high ionic strength (especially  $\text{NaNO}_3$  solutions), temperature, and saturation state. Dissolution of the sediment minerals primarily provides the source of dissolved Si necessary for precipitation of secondary phases.

Second, we will proceed in quantifying and characterizing the nucleation mechanisms for secondary precipitates. Understanding nucleation mechanism, nucleation sites on soils minerals, and the role of reactive surface area in simultaneous dissolution and precipitation reactions are key unknown components in comprehending this contaminated vadose zone system. Previous work on the generation of colloids by reaction of Hanford sediments with tank simulants had indicated that homogeneous nucleation may be important at Hanford at least under the relatively high flow rate conditions of the column experiments. However, field evidence for substantial colloid transport is still lacking. Our previous work suggests that nucleation on mineral substrates may be just as important and that secondary phase overgrowths can passivate primary mineral surfaces and prevent their dissolution as well as cement sediment grains together. It is likely that secondary phases also remove contaminants from solution, by incorporation in the secondary phase structure or by formation of reduced metal solids.

Third, the extent of simultaneous uptake or release of contaminants during primary phase dissolution, secondary phase precipitation, and subsequent secondary phase dissolution needs to be determined and correlated to the reaction kinetics. We intend to focus on understanding the extent of irreversibility of Cs and U uptake in secondary phases using a radiochemical counting approach coupled with characterization of powdered and single crystal mineral samples.

Our data will provide fundamental information useful for (1) comprehending the unsampled sub-tank sediments particularly with respect to as yet undetermined mass balances for the full distribution of released radionuclides, (2) estimating the conditions of formation and stability of colloidal and surface

precipitates, and (3) predicting the future mobility of contaminants incorporated in precipitated via dissolution reactions.

**This project began in 2002. The first progress report is expected in late 2003.**

# **Environmental Management Science Program Research in Washington**

## **University of Colorado**

### **86900 - Influences of Flow Transients and Porous Medium Heterogeneity on Colloid-Associated Contaminants Transport in the Vadose Zone**

**Principal Investigator:** Dr. Joseph Ryan

**Problem Area:** Subsurface Contamination

Associations between contaminants and soil colloids have affected contaminant mobility in the vadose zone and the quality of underlying groundwater in several settings. Nevertheless, the factors governing colloid-facilitated contaminant transport in unsaturated porous media have not been rigorously explored nor formalized into a quantitative model. In particular, the roles of flow transients and porous medium heterogeneity in colloid transport and colloid-associated contaminant transport have not been adequately investigated to date.

We propose to examine the enhanced transport of radionuclides by mineral colloids within variably saturated media. We will conduct laboratory experiments with porous medium micromodels to identify mechanisms that govern colloid mass transfer interactions (i.e., deposition and mobilization) at solid-water and air-water interfaces. We hypothesize that thin film straining and solid-water interface reactions dominate the deposition of soil colloids under unsaturated conditions, while expansion of thin-water films and elevated shear forces in the vicinity of the mineral grains drive colloid mobilization during periods of transient flow. The kinetics of adsorption and desorption reactions between radionuclides ( $^{137}\text{Cs}$  and  $^{90}\text{Sr}$ ) and the mineral colloids (illite clay and silica) will be measured, and the relationships between radionuclide-colloid interactions and contaminant mobility will be elucidated in column experiments with unsaturated media. We believe that the kinetics of contaminant desorption from colloids will determine the extent to which colloid-facilitated transport contributes to the overall transport of radionuclides. Special attention will be devoted to defining the influences of porewater-flow transients and structured heterogeneities (i.e., preferential flow paths) on the mobilization and subsequent migration of colloid-bound radionuclides. We will perform experiments with columns containing well-defined heterogeneities and with intact cores collected from sites within the DOE complex.

Knowledge gleaned from each phase of the laboratory work will be used to develop a mathematical model appropriate for quantifying colloid-facilitated contaminant transport in variably saturated media. Tests of the mathematical model against data from the column experiments will yield functional relationships between model parameters governing colloid and radionuclide mass transfer and measure system properties. The significant environmental implications of colloid-facilitated transport in the vadose zone make experimental observations and development of a quantitative understanding of the phenomenon critically important. Our proposed work represents the first systematic approach to identifying the controls on colloid-associated transport through unsaturated, heterogeneous media under transient flow conditions.

**This project began in 2002. The first progress report is expected in late 2003.**

# Environmental Management Science Program Research in Tennessee

## Oak Ridge National Laboratory

### 86911 - Coupled Geochemical and Hydrological Processes Governing the Fate and Transport of Radionuclides and Toxic Metals Beneath the Hanford Tank Farms

**Principal Investigator:** Dr. Philip M. Jardine

**Problem Area:** Subsurface Contamination

The overall goal of this research is to provide an improved understanding and predictive capability of coupled hydrological and geochemical mechanisms that are responsible for the accelerated migration and immobilization of radionuclides and toxic metals in the vadose zone beneath the Hanford Tank Farms. The study is motivated by the technological and scientific needs associated with the long-term management of the enormous in-ground inventories of multiple contaminants at the Hanford site. The work complements and builds upon our recent EMSP project 70219 which provided new insights into the hydrological mechanisms controlling solute migration in the Hanford vadose zone. The objectives of the proposed work are (1) to provide an improved understanding of how preferential vertical and lateral flow, and the formation of immobile water influence the transport of radionuclides and toxic metals (i.e.  $^{235/238}\text{U}$ ,  $^{99}\text{Tc}$ ,  $^{60}\text{Co}$ , and  $\text{Cr(VI)}$ ) in heterogeneous, laminated sediments, (2) to quantify the rates and mechanisms of radionuclide and toxic metal interaction with the solid phase under various hydrologic conditions, and (3) provide new insights into how physical and mineralogical heterogeneities (e.g. stratification, pore regime connectivity, mineral composition along flowpaths) influence contaminant retardation and the degree of geochemical nonequilibrium during transport. The proposed work consists of three multidisciplinary tasks that seek to resolve several scientifically-rigorous hypotheses concerned with coupled hydrological and geochemical processes controlling contaminant migration in the vadose zone. Our approach involves (1) field-relevant, long-term unsaturated flow and transport experiments in undisturbed Hanford sediments, (2) an experimental design configuration that provides the ability to delineate complex geochemical processes, such as redox transformations and sorption, in different sediment pore regimes during reactive contaminant transport, (3) a multiple tracer strategy, similar to our recent EMSP research, for quantifying preferential flow and nonequilibrium mass transfer processes at various water contents, (4) the use of novel surface analyses techniques (e.g. x-ray absorption spectroscopy, micro-Raman, Mossbauer spectroscopy) to quantify the distribution and chemical environment of contaminants as a function of sediment lithology and water content, and (5) the use of existing coupled processes transport models for simulating the mobility and geochemical reactivity of contaminants at various water contents. The experimental and numerical results from this research will provide knowledge and information in previously unexplored areas of vadose zone fate and transport to support the Hanford Integration Project's performance/risk assessment and decision-making process for Tank Farm restoration.

By unraveling fundamental contaminant transport mechanisms in complex porous media, we will provide an improved conceptual understanding and predictive capability of a variety of vadose issues within the DOE system. Further, this proposal combines DOE's commitment to environmental restoration with its commitment to major user facilities (Stanford Synchrotron Radiation Laboratory, Advanced Photon Source, Environmental Molecular Sciences Laboratory) and academic education (Stanford University, ORISE).

**This project began in 2002. The first progress report is expected in late 2003.**

# **Environmental Management Science Program Research in Tennessee**

## **Oak Ridge National Laboratory**

### **86912 - Nanofluidic Structures for Electrokinetic-Based Hydraulic Pumps**

**Principal Investigator:** Dr. J. Michael Ramsey

**Problem Area:** Subsurface Contamination

We propose to develop both low and high pressure pumps on microfluidic devices that can be used for subsurface sampling of contaminants, concentrating the contaminants by solid phase extraction, and analyzing the contaminants with chromatographic separations. The small, low cost devices that will be possible, if this project is successfully completed, will address a broad range of water borne analytes including volatile and nonvolatile organics and heavy metals. The technology will be applicable to field and remote monitoring measurements scenarios. To date, microfabricated pumps have used mechanical means, e.g., membranes and pistons, to move fluids and demonstrated marginal performance including poor reliability, low-pressure generation, and high power consumption. The proposed pumping element will overcome these limitations by using electroosmotic flow to generate superambient pressures to sample contaminants from the environment and superambient pressures to perform solid phase extraction and chromatographic separations. The pump will use an electric potential to drive the fluid and two nanofabricated elements to generate the pressure and terminate the electric field. The focus of the project will be developing and optimizing the geometry and surface chemistry of the nanofabricated elements. These pumps will be capable of generating pressures in the range of 1 to 100 bar with flow velocities from 0.01 to 10 mm/s. By successfully developing these pumps, we will further efforts to produce inexpensive instrumentation that can be used for hand-held or remote monitoring to assess subsurface transport, site remediation, and validation needs.

**This project began in 2002. The first progress report is expected in late 2003.**

# **Environmental Management Science Program Research in California**

## **Lawrence Berkeley National Laboratory**

### **86922 - Characterization of Coupled Hydrologic-Biogeochemical Processes Using Geophysical Data**

**Principal Investigator:** Dr. Susan Hubbard

**Problem Area:** Subsurface Contamination

Biogeochemical and hydrological processes are naturally coupled and variable over a wide range of spatial and temporal scales. Additionally, many remediation approaches also induce dynamic transformations in the system. It is widely accepted that effective remediation requires a better understanding of coupled processes than is currently available. Further complicating the problem is the inability to collect the necessary measurements at a high enough spatial resolution yet over a large enough volume for understanding field-scale transformations.

Our proposed research includes:

1) Improving the understanding of coupled processes and 2) Investigating the capability to characterize and monitor coupled processes at appropriate resolutions and spatial scales using geophysical data.

We propose to monitor lab and field-scale system perturbation experiments using microbial, geochemical, hydrological, and geophysical (seismic, electrical, radar) measurements. The resulting measurements will provide the database necessary for investigating coupled processes. With this data, we will also investigate the sensitivities of the different geophysical attributes to system transformations.

The combined experimental, theoretical, and numerical analysis will produce many benefits to EMSP, including:

- Development of coupled-process models through experimental studies at variable scales and complexities that account for the interacting physical, chemical and biological processes that govern transport and remediation
- Development of geophysical approaches for characterizing and monitoring the physical, chemical and biological processes of the subsurface and the changes in those coupled processes over time.

These developments will reduce the uncertainty currently associated with remediation approaches, which will in turn reduce the time and cost required for EM to achieve their remediation goals.

**This project began in 2002. The first progress report is expected in late 2003.**

# **Environmental Management Science Program Research in Washington**

## **Pacific Northwest National Laboratory**

### **86952 - Multi-Regional Reactive Transport Due to Strong Anisotropy in Unsaturated Soils with Evolving Scales of Heterogeneity**

**Principal Investigator:** Dr. Anderson L. Ward

**Problem Area:** Subsurface Contamination

Standard practices for predicting reactive transport under unsaturated conditions do not account for the random heterogeneity and strong anisotropy that can be expected under the extremes of nonlinear flow behavior typical of the vadose zone at the Department of Energy's (DOE) Hanford Site. Variable anisotropy, an extreme of nonlinear behavior, can both subdue and enhance predicted migration rates depending on local stratigraphy, enhance nonequilibrium flow, limit access to reactive surfaces, and lead to the costly over-engineering of remediation and risk-management strategies. Even though lateral flow due to variable anisotropy has dominated every field experiment (both planned and unplanned) performed at the Hanford Site, it is unaccounted for in all but a few models. Those models that do consider lateral flow are formulated on the presumption that flow can be linearized and treated as a small perturbation to the unsaturated flow dynamics and, therefore, are in contradiction of our prevailing knowledge of field manifestations. Nonequilibrium mass transfer in strongly anisotropic soils is an example of macroscopic averaging of a disordered dynamical process where the dominant physical process depends on the scale over which it is averaged. In this project, we propose to investigate precisely a range of microscopic flow regimes and measure accurately their three-dimensional average properties. Undisturbed cores from major sedimentary facies will be used to quantify pore morphology and the topology, pore-scale anisotropy, and mobile-immobile partitioning of water. Morphology data will be used to generate a hierarchical pore-scale model, with exactly specified physics, to simulate flow and to find suitably averaged (up-scaled) parameters to describe macroscopic transport with continuum models. A research centrifuge will be used to investigate the application of up-scaled parameters to processes that occur under transient flow and at impracticably large spatial and temporal scales. The results of this investigation will bridge the gap between pore-scale fluid migration and large-scale displacement behavior and, thereby, will improve our prediction capability for systems characterized by strong anisotropy. Without improved conceptualizations, remediation and risk-management strategies will be over-engineered at great expense, and corrective and remedial actions will be indefensible.

**This project began in 2002. The first progress report is expected in late 2003.**



# **Environmental Management Science Program Research in Idaho**

## **Idaho National Engineering and Environmental Laboratory**

### **86977 - Multiphase Flow in Complex Fracture Apertures Under a Wide Range of Flow Conditions**

**Principal Investigator:** Dr. Paul Meakin

**Problem Area:** Subsurface Contamination

At several DOE sites and in other countries, pollutants have traveled in the vadose zone much further and faster than predicted. This reveals the inadequacies of both the computer models used to predict the transport of pollutants in the subsurface and the conceptual models on which they are founded. We propose filling important knowledge gaps and developing new conceptual models to understand how pollutants travel in the vadose zone. We have planned a closely coordinated experimental and computer modeling program to study multiphase flow in fracture apertures. We will test the hypothesis that focusing flow onto preferred pathways (such as fracture apertures), intermittent flow conditions, and the colloid mediated transport of strongly adsorbed pollutants play an important role in rapidly transporting subsurface contamination. We will perform experiments and simulations using several modeling methods, both under a wide range of flow conditions in realistic, complex fracture apertures (computer-generated fracture apertures using both fractal and nonfractal statistical models, well-characterized natural fractal apertures, and/or replicas of natural fracture apertures). Our modeling program will be based on methods that are well suited to geometrically complex boundary conditions (realistic fracture aperture geometries) and complex moving interfaces. These methods include lattice-gas/lattice-Boltzmann models, invasion percolation models, molecular dynamics, and smoothed particle hydrodynamics. By using these various methods, we can evaluate different modeling approaches and use computer modeling to extrapolate and interpolate the experiments to a broader range of conditions. We will perform the experiments in a unique and versatile matched-index-of-refraction flow laboratory at INEEL.

**This project began in 2002. The first progress report is expected in late 2003.**

# Environmental Management Science Program Research in Idaho

## Idaho National Engineering and Environmental Laboratory

### 86981 - Transport, Targeting and Application of Functional Nanoparticles for Degradation of Chlorinated Organic Solvents

**Principal Investigator:** Dr. George Redden

**Problem Area:** Subsurface Contamination

Over the past decade, laboratory and field studies have demonstrated that zero-valent iron and bimetallic colloids combined with noble metal catalysts can rapidly transform dissolved chlorinated organic solvents into non-toxic compounds. This emerging technology also has the potential to address Dense Non-Aqueous Phase Liquid (DNAPL) contamination, one of DOE's primary contamination problems. We propose to develop and prove a technology to more effectively remediate chlorinated solvents that are present as DNAPLs in the subsurface. A variety of nanoparticles consisting of Fe(0) and a noble metal catalyst such as Pd or Pt, will be prepared individually and as composites, and tested for reaction efficiency. The nanoparticle surfaces will then be modified with amphiphilic copolymers that maintain a stable suspension of the particles in either aqueous or organic solvents for transport in a porous matrix, and create an affinity for the water-DNAPL interface. The particle mobility, targeting capabilities, and DNAPL degradation rates will be tested both in micro-model flow cells and in larger two-dimensional experiments that are representative of subsurface properties at contaminated DOE sites. A transport model that incorporates hydrodynamic parameters and solid-solution interfacial properties, as functions of physical and chemical conditions in the porous matrix, will also be developed. The objective of this research is to provide an improved technology to reduce or eliminate a recalcitrant and persistent source for groundwater contamination by chlorinated solvents. Additional benefits will be to advance the use of synthetic nanoparticles engineered for specific functions in subsurface environments, and to improve our ability to manipulate the migration of natural colloids that cause subsurface transport of many DOE-relevant contaminants.

**This project began in 2002. The first progress report is expected in late 2003.**

# Environmental Management Science Program Research in Arizona

## University of Arizona

### 86984 - Caustic Waste-Soil Weathering Reactions and Their Impacts on Trace Contaminant Migration and Sequestration

**Principal Investigator:** Dr. Jonathan Chorover

**Problem Area:** Subsurface Contamination

The mobility of radionuclides ( $^{137}\text{Cs}$ ,  $^{90}\text{Sr}$ ,  $^{129}\text{I}$ ) in the vadose and saturated zones is controlled by interactions with natural soil particles. High surface area clay minerals and metal oxides are particularly important sorbents in soils at Department of Energy (DOE) sites (e.g., Hanford Site, Savannah River Site) that are impacted with radionuclide and metal contaminants. However, clays are also susceptible to weathering-induced transformations during near-field exposure to the high pH, high Al and high ionic strength conditions of liquid tank wastes that have been released into the subsurface. Although clay dissolution may diminish soil sorption capacity in some cases, *our prior research has indicated that precipitation of neoformed "secondary" phases results in time-dependent sequestration of Cs and Sr into increasingly recalcitrant forms in both specimen clay systems and bulk Hanford sediments.* We conducted integrated macroscopic, microscopic and spectroscopic studies on a suite of specimen clay minerals (illite, vermiculite, smectite and kaolinite) and Hanford sediments (Hanford Formation, Ringold Formation) reacted with synthetic tank waste leachate (STWL) solutions containing relevant concentrations of Cs and Sr. Dissolution of Si was found to result in incipient precipitation of short-range-ordered Al and Si phases that transform to crystalline zeolites, with concurrent impacts on Cs and Sr uptake kinetics. Mineralogical changes occurring *in-situ* at the Hanford site also suggest the accumulation of Na-bearing zeolites and short-range-ordered minerals. Our lab studies have shown that these mineral transformations strongly impact Cs and Sr uptake (monitored using wet chemical, solid-state NMR, XRD, FTIR, SEM-EDX and TGA methods) and they will also likely impact iodine ( $^{129}\text{I}$ ) uptake (not previously measured). The transformations depend on (i) the type of clay mineral and (ii) contaminant concentrations. The formation of radionuclide-containing zeolites occurs on the time scale of months in our experiments. Increased recalcitrance of Cs and Sr to desorption accompanies increasing crystallinity of secondary solids (consistent with Ostwald ripening) for all systems studied. The neoformed solids are colloidal, but their mobility is limited by flocculation in the high ionic strength STWL solution.

The proposed research will assess the extent to which caustic waste-soil weathering contributes to stabilization versus enhanced migration of contaminants in the vadose zone. The main objectives of this work are to (1) measure the coupling of clay mineral weathering and contaminant uptake kinetics over an expanded range in aqueous geochemistry and soil moisture content (saturation) representing a gradient from near-field to far-field conditions; (2) determine the molecular structure of contaminant binding sites and their change with weathering time during and after exposure to STWL; (3) establish the stability of neoformed weathering products and their sequestered contaminants upon exposure of the solids to more "natural" soil solutions (i.e., after removal of the caustic waste source); and (4) integrate macroscopic, microscopic and spectroscopic data to distinguish labile from non-labile contaminant binding environments, including their dependence on system composition and weathering time.

Laboratory experiments will be conducted using batch, stirred-flow and column (saturated and unsaturated) designs. Dissolution-precipitation and contaminant uptake/release will be tracked using ICP-AES, ICP-MS, ion chromatography and  $\alpha$  counting (for radioisotope tracers). Mineral transformations will be monitored with XRD, TGA, SEM/EDS and FTIR spectroscopy. X-ray absorption and NMR spectroscopies will be used to elucidate molecular-scale contaminant binding interactions and their dependency on reaction conditions and aging time. Stability of neoformed, contaminant-bearing solids will be determined. The Co-PIs will combine complementary expertise in soil chemistry, geochemistry and spectroscopy to continue collaborative research on contaminant sequestration in the subsurface.

**This project began in 2002. The first progress report is expected in late 2003.**

# **Environmental Management Science Program Research in Vermont**

## **New England Research, Inc.**

### **86989 - Heterogeneity and Scaling in Geologic Media: Applications to Transport in the Vadose and Saturated Zones**

**Principal Investigator:** Dr. Stephen R. Brown

**Problem Area:** Subsurface Contamination

We propose a comprehensive study of heterogeneity and scaling of the structure of geologic media from sub-millimeter (pore) scale to the meter scale. We focus on measurement of this structure through geophysical methods, synthesis and description through mathematical models, and the implications for flow and transport in the vadose and saturated zones. We primarily focus on soil and sedimentary materials, but consider some aspects of fracture geometry in rocks and soils.

To accomplish these goals, we will (1) perform multi-scale measurements of heterogeneity and scaling of physical properties in the laboratory and at the backyard field scale, 2) describe and synthesize the data and develop mathematical models, and 3) perform parameter studies to explore these models in the context of transport in the vadose and saturated zones.

In the course of this project we will develop a substantial data set for each of the samples we study. The data set will include extensive physical properties measurements, imagery, source information and characterization. We will assemble the appropriate data for each sample together with sufficient auxiliary documentation to characterize both the sample and the data in the collection and make the results freely available.

The DOE National Laboratories have extensive environmental remediation and operations centers as well as research teams specializing in environmental problems. These organizations are concerned largely with pollution prevention, safe disposal of hazardous materials, polluted site identification and characterization, and cleanup of polluted sites. These organizations, and the private-industry subcontractors they hire, require state of the art tools and techniques for characterization and monitoring. Our research will contribute to the effort by providing descriptions of heterogeneities and scaling properties in the vadose and saturated zones with particular emphasis on flow and transport. This work will also provide an important link between some geophysical measurements and fluid transport characteristics.

**This project began in 2002. The first progress report is expected in late 2003.**

# **Environmental Management Science Program Research in Colorado**

## **U.S. Geological Survey - Denver**

### **86992 - Improving Ground Penetrating Radar Imaging in High Loss Environments by Coordinated System Development, Data Processing, Numerical Modeling, and Visualization Methods with Applications to Site Characterization**

**Principal Investigator:** Dr. David L. Wright

**Problem Area:** Subsurface Contamination

Ground penetrating radar (GPR) is a geophysical tool with the potential to locate, identify, and measure subsurface heterogeneity features directly. Unfortunately, in many environments the method does not produce interpretable data. There are a number of unstated assumptions that are usually made with GPR. One is that the radiated pulse output from the antenna into the ground does not change significantly in shape or amplitude across a given profile. Another is that propagation through the ground occurs such that reflections from subsurface interfaces will be replicas of the radiated waveform. Under many earth conditions these assumptions may be violated, leading to reflection arrivals that are misinterpreted or uninterruptible. Dispersion, frequency dependent velocity, is caused by high electrical conductivity and/or high dielectric or magnetic relaxations, and results in waveform changes during propagation such that the reflected arrivals are not replicas of the radiated waveform. Scattering of energy by an abundance of randomly oriented interfaces can also cause misinterpreted waveform changes. Variations in the very near surface conditions around a ground-coupled antenna as it moves along a profile will change the shape of the radiated waveform it transmits into the subsurface. When these changes are unknown, they cause misinterpretations of far field reflection events. Environments that result in these problems are also almost always associated with high signal attenuation.

Although the laws of physics will always impose limits to what can be achieved, we do not think that all that can be done has been done to produce correctly interpreted GPR data acquired in challenging environments. Specifically, we propose to extend the limits of performance of GPR in both the hardware domain and in the numerical computation domain. The key features in our system include 1) greater dynamic range through real time sampling and receiver gain improvements, 2) modified, fully characterized antennas with current sensors to allow dynamic measurement of the changing radiated waveform, 3) modified deconvolution and depth migration algorithms exploiting the new antenna output information, 4) development of automatic full waveform inversion made possible by the known radiated pulse shape, 5) a modified visualization package for efficient subsurface interpretation. It is our contention that an approach such as the one we propose here can sharpen subsurface images and extend possible depths of investigation in ways that are not now available in the GPR community. Since GPR is such a powerful field tool with a unique subsurface characterization potential, an extension of the domain of applicability of GPR is a worthy research goal.

**This project began in 2002. The first progress report is expected in late 2003.**

# **Environmental Management Science Program Research in Idaho**

## **University of Idaho**

### **87003 - Advanced Conceptual Models for Unsaturated and Two-Phase Flow in Fractured Rock**

**Principal Investigator:** Dr. Michael J. Nicholl

**Problem Area:** Subsurface Contamination

The Department of Energy (Environmental Management Program) is faced with two major issues involving two-phase flow in fractured rock; specifically, transport of dissolved contaminants in the Vadose Zone, and the fate of Dense Nonaqueous Phase Liquids (DNAPLs) below the water table. Conceptual models currently used to address these problems do not correctly include the influence of the fractures, thus leading to erroneous predictions. Recent work has shown that it is crucial to understand the topology, or 'structure' of the fluid phases (air/water or water/DNAPL) within the subsurface. It has also been shown that even under steady boundary conditions, the influence of fractures can lead to complex and dynamic phase structure that controls system behavior, with or without the presence of a porous rock matrix. Complicated phase structures within the fracture network can facilitate rapid transport, and lead to a sparsely populated and wide spread distribution of concentrated contaminants; these qualities are highly difficult to describe with current conceptual models.

We propose the development of advanced conceptual models for two-phase flow in fractured rock. Our approach is founded on systematic experimentation. As preliminary experiments have shown that behavior at fracture intersections is key, we will begin by conducting systematic experimentation to identify and classify behavior at intersections. Understanding gained at the scale of intersections will be used to augment a Modified Invasion Percolation Model (MIP) that has shown significant promise in predicting flow through fracture networks. Development of the MIP model will be iterative, in that we will use numerical simulations to design critical physical experiments at the network scale which will challenge the model. The augmented, and fully tested MIP model will be exercised on realistic fracture networks for the purpose of understanding large-scale development of phase structure. Networks will be generated using algorithms conditioned to field data collected at DOE sites (e.g., INEEL, Nevada Test Site, Oak Ridge). Results of the large-scale network simulations will be abstracted so that critical features may be included in conceptual models used by the Environmental Management Program.

**This project began in 2002. The first progress report is expected in late 2003.**

# Environmental Management Science Program Research in Idaho

## University of Idaho

### 87016 - Trace Metals in Groundwater & Vadose Zone Calcite: In Situ Containment & Stabilization of <sup>90</sup>Sr and Other Divalent Metals & Radionuclides at Arid West DOE

**Principal Investigator:** Dr. Bob W. Smith

**Problem Area:** Subsurface Contamination

Radionuclide and metal contaminants are present in the vadose zone and groundwater throughout the U.S. Department of Energy (DOE) weapons complex. *In situ* containment and stabilization of these contaminants in vadose zones or groundwater is a cost-effective treatment strategy. However, implementing *in situ* containment and stabilization approaches requires definition of the mechanisms that control contaminant sequestration. One mechanism for metals and radionuclides is co-precipitation in authigenic calcite and calcite overgrowths. Calcite, a common mineral in many aquifers and vadose zones in the arid western U.S., can incorporate divalent metals such as strontium, cadmium, lead, and cobalt into its crystal structure by the formation of solid solutions. The rate at which trace metals are incorporated into calcite is a function of calcite precipitation kinetics, adsorption interactions between the calcite surface and the trace metal in solution, solid solution properties of the trace metal in calcite, and also the surfaces upon which the calcite is precipitating. A fundamental understanding of the coupling of calcite precipitation and trace metal partitioning and how this occurs in aquifers and vadose environments is lacking.

The objectives of this research are to: **a) elucidate the mechanisms and rates for the release of sorbed trace metals and their subsequent sequestration by co-precipitation in calcite induced by urea hydrolysis, b) evaluate at the field scale the influence of microbial calcite precipitation on the partitioning and retention of strontium and other naturally occurring divalent metals in groundwater, and c) identify specific microbial community characteristics that signify subsurface geochemical conditions conducive to calcite precipitation.**

These objectives will be accomplished by conducting integrated field and laboratory research evaluating a) the precipitation rate of calcite through *in situ* experiments and b) the partitioning of strontium and other metals into carbonate minerals through laboratory experiments and field characterization. The field-based research will focus on an uncontaminated Idaho National Engineering and Environmental Laboratory (INEEL) site with hydrogeological features similar to the <sup>90</sup>Sr contaminated groundwater and perched-water vadose zone site at the Idaho Nuclear Technology and Engineering Center (INTEC). In addition a limited investigation relevant to the Hanford I 100-N area is proposed for later stages of the project.

The experimental focus will be on the *in situ* microbially-catalyzed hydrolysis of urea, which results in an increase in pH and carbonate, and precipitation of calcite. The parameters for the field experiments will be developed in laboratory batch and column experiments with known urea-hydrolyzing microorganisms in order to evaluate the relative importance of environmental factors (e.g., pH, metals, urea concentration, microbial presence, flow rates) on the precipitation of calcite and the sequestration of metals. Single well "push-pull" experiments using urea and urease or an electron donor (to stimulate the *in situ* microbial community) will be used to evaluate *in situ* calcite precipitation in the subsurface. These experiments will include the formation of calcite overgrowths onto mineral templates. The trace metal concentrations will be determined using highly sensitive laser ablation - inductively coupled plasma - mass spectrometry (LA - ICP- MS). By evaluating urea hydrolysis through both direct injection of urease as well as stimulating naturally occurring subsurface ureolytic microorganisms, we anticipate results that will allow the determination of feasibility of the *in situ* containment and stabilization approach under conditions of short-term intense subsurface manipulation as well as longer term "natural attenuation" based approaches. Using traditional cultivation-based microbiological as well as molecular methods, we will also determine biological indicators of urea hydrolysis as a means of verifying that the observed precipitation of calcite is indeed correlated with urea hydrolysis.



**This project began in 2002. The first progress report is expected in late 2003.**

# Environmental Management Science Program Research in Illinois

## University of Illinois at Urbana-Champaign

### 87023 - A New Framework for Adaptive Sampling and Analysis During Long-Term Monitoring and Remedial Action Management

**Principal Investigator:** Dr. Barbara S. Minsker

**Problem Area:** Subsurface Contamination

**Introduction and Objectives:** DOE and other Federal agencies are making a significant investment in the development of field analytical techniques, nonintrusive technologies, and sensor technologies that will have a profound impact on the way environmental monitoring is conducted. Monitoring and performance evaluation networks will likely be based on suites of in situ sensors, with physical sampling playing a much more limited role. Designing and using these types of networks effectively will require development of a new adaptive paradigm for sampling and analysis of remedial actions, which is the overall goal of this project. Specifically, the objectives of this project are to: (1) enable effective interpretation of non-intrusive monitoring data, (2) improve predictions and assessment of remediation performance, (3) develop decision rules for on-site adaptive sampling and analysis, and (4) enable more informed decision making and risk analysis of long-term monitoring systems.

**Research Plan and Methodology:** These objectives will be accomplished through development of a new framework for adaptive sampling and analysis, decision making, and risk assessment. The framework assumes that existing data have been used to develop some type of conceptual model for the site, be it an analytical, numerical, or statistical model. This project will test the effectiveness of new hierarchical models that integrate all sources of process knowledge at the site, including geological data collected during site characterization, measurements of parameters collected during routine groundwater monitoring (including surrogate data and data at different spatial and temporal resolutions), and scientific understanding of biochemical transformation processes. An interactive model and parameter identification system will also be developed for creating the new models efficiently. The models would then be used to predict future measurements, to identify initial sampling plans, and to create decision rules for adaptive, on-site sampling and analysis. During a particular sampling episode, initial measurements would be compared with predictions and statistically significant deviations would be identified. The decision rules would then be used to identify further sampling needs. This process would be repeated until sufficient data has been collected to verify any anomalies observed and reduce uncertainties to acceptable levels. At the end of the sampling period, or during periodic reviews, the monitoring objectives, conceptual model, initial sampling plans, and decision rules would be re-evaluated and updated to incorporate knowledge obtained from the new sampling data and to accommodate changing site needs. Methods will be developed for automated updating of these components of the framework (with or without user interaction) to ensure efficiency and cost-effectiveness. Our framework will be tested using data from the 317/319 areas at Argonne National Laboratory, where a traditional pump-and-treat and novel phytoremediation system are in place to control off-site migration of a tritium and VOC plume. To enable rigorous testing and comparison of methods, the framework will initially be tested using synthetic data generated based upon historical trends observed at the site. Once the initial testing and methods development is completed, the framework will be validated using the most recent available data from the 317/319 area and used to identify: (1) long-term mass measurement trends, (2) future data needs for assessing the performance of the pump-and-treat and phytoremediation systems, and (3) key measurements for model validation.

**Relevance to DOE:** In a report to Congress, DOE estimated that it would spend approximately five and a half billion dollars on long-term site management ("stewardship") over the six years between 2000 and 2006 (DOE, 2001). The report also states that long-term stewardship costs will be more than 100 million dollars per year over the next 70 years. With these significant costs, it is critical that long-term monitoring and management be as efficient and effective as possible. The framework proposed in this project is expected to contribute substantially to reducing costs and increasing effectiveness of data collection and

analysis. Specifically, this project will address the following subsurface contamination research needs stated in this notice inviting grant applications:

- Conceptual modeling: Innovative methods will be developed for efficiently integrating all process knowledge at all scales into conceptual models. The methods will be tested and validated at a DOE site, ensuring relevance to the kinds of subsurface environments and contamination problems encountered at DOE sites.
- Monitoring and validation: The methods developed in this project will be created to: (1) design monitoring systems to detect both current conditions and changes in system behavior, (2) allow validation and updating of models using present-day measurements, (3) identify key measurements for model validation, including surrogate data and data at different spatial and temporal resolutions, and (4) identify trends in measurements over long time periods.

**This project began in 2002. The first progress report is expected in late 2003.**

# Environmental Management Science Program Research in Missouri

## University of Missouri - Kansas City

### **88615 - Investigating the Potential for Long-Term Permeable Reactive Barrier (PRB) Monitoring from the Electrical Signatures Associated with Reduction in Reactive Iron Performance**

**Principal Investigator:** Dr. Lee D. Slater

**Problem Area:** Subsurface Contamination

We will conduct the fundamental research required to develop an electrical approach to long-term noninvasive monitoring of the performance of permeable reactive barriers (PRBs). We submit that distinct electrical signatures result as the performance of reactive iron in chlorinated solvent degradation is reduced over time. We also propose that PRBs are unique environmental targets for electrical imaging. We will conduct synthetic studies in order to define optimal field acquisition and data modeling parameters for the case of a PRB. A field test at a well-characterized PRB will be performed over a three-year period. We anticipate that this proof-of-concept test will illustrate the practical utility of this technology.

Basic laboratory research on the electrical properties of reactive iron systems during chlorinated solvent treatment forms the main component of this proposal. We will measure frequency dependent electrical properties between 0.1-1000 Hz. In this range, electrical properties are controlled by ionic conduction through the electrolyte, surface electronic or ionic conduction, as well as diffusion mechanisms that occur at the mineral surface- pore fluid interface. The surface area of reactive iron exposed to contaminated groundwater exerts a primary control on PRB performance. Iron oxidation and precipitation onto the iron surface both reduce reactivity and are detrimental to PRB performance. Our fundamental assertion is that low frequency electrical measurements are sensitive to these changes in surface area and surface chemistry. We will test this concept by simulating a PRB in a laboratory column and accelerating reaction rates to make measurements on manageable time scales. We will monitor the electrical response during trichloroethylene (TCE), perchloroethylene and dichloroethane (DCE) degradation. Geochemical indicators of PRB performance (chlorinated solvent concentration, Eh, pH, DO, cations indicative of precipitation) will be determined to constrain interpretation of electrical signatures. Following completion of monitoring, we will disassemble columns and visually assess iron oxidation and precipitates formed. This basic research will define key mechanisms attributing to the time-varying electrical response of reactive iron during chlorinated solvent degradation.

We will perform a detailed analysis of synthetic data, coupled with inverse algorithm development, to optimize application of electrical imaging in long-term PRB monitoring. The PRB is a unique electrical target: we will conduct sensitivity analyses to optimize field acquisition parameters and investigate incorporation of constraints to improve inverse algorithm performance in PRB image reconstruction. A long-term field test of electrical imaging monitoring will be conducted at a well- characterized, active PRB at the Kansas City DOE facility. We will conduct 3-D, complex resistivity imaging between boreholes drilled on either side of this barrier. Key geochemical indicators of PRB performance will be monitored using currently existing wells installed around and within this barrier. In the third year of the study, we will conduct angle coring at locations determined by electrical imaging results. Appropriate geochemical and microbiological analyses will be performed to verify the causes of PRB degradation identified with electrical imaging and geochemical analyses.

**This project began in 2002. The first progress report is expected in late 2003.**